# Geochimica et Cosmochimica Acta

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# GEOCHIMICA ET COSMOCHIMICA ACTA



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# The next decade in geochemistry*

EARL INGERSON
U.S. Geological Survey, Washington, D.C.

(*Received* 10 *December* 1957)

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* Address of the retiring President of the Geochemical Society given at the second Annual Meeting of the Society in Atlantic City, New Jersey, November 4, 1957.

**Abstract**—The purpose, associations, functions, and activities of the Geochemical Society are reviewed briefly. Work on the Colorado Plateau uranium deposits is described as an example of what geochemical research, in conjunction with detailed field work, mineralogical studies, and related techniques can contribute to the understanding of a type of deposit. It is pointed out that not only have these studies given a great deal of information about the origin of the ores, but they have brought about directly a manifold increase in production and reserves of uranium in the United States. Indirectly, they aided the discovery of the tremendous deposits of the Blind River area in Ontario.

It is suggested that similar broad cooperative attacks could not only yield comparable results with other types of mineral deposits, such as laterites and Mississippi Valley type lead–zinc deposits, but could also advance our knowledge and understanding of such diverse problems of geology and cosmology as the origin of granites, origin and geologic implications of meteorites (including tektites), origin and search for petroleum, and geochemical relations and interpretations of natural waters. For each of these problems methods of approach are outlined and for some of them, specific projects and correlative problems are mentioned.

It is further suggested that the broad cooperative attack needed for most of these problems might be fostered most effectively by a programme comparable to that of the I.G.Y., even though for most types of geochemical research synoptic sampling and observations are not as important as they are for many projects in geophysics.

## Introduction

### *The Geochemical Society*

The word "society" means many things to different people. Webster's unabridged dictionary gives twelve different principal meanings and seven subordinate definitions. Only one of these definitions, "participation (by) cooperation", has any dynamic significance, and this one is called *obsolete*. Our English definitions, it appears, have come to emphasize the fraternal aspects of a coming together, without much regard for the *purpose* of getting together.

In a pre-war dictionary published in Buenos Aires there is a definition that fits much better my idea of what a scientific society ought to be. It says that "a society is a group of people who *attain an end* by mutual cooperation". Nothing is said of form, or organization; the idea is getting something done. Under this definition the Geochemical Society does not qualify as a society until its members collectively have set for themselves specific objectives and have made substantial progress toward attaining them.

With this in mind let us review briefly what objectives the Society has set for itself, what advances have been made in those directions, and what additional programmes the Society should undertake to enable it to stand among the effective and productive scientific societies of the world.

The object of the Society, as stated in the constitution is "to encourage the application of chemistry to the solution of geological and cosmological problems". This is a broad statement of purpose and is incapable of consummation; for an evaluation of accomplishment we must look at limited objectives.

*Associations.* As indicated above, a fundamental property of a society is cooperation among the individuals who compose it. Just as important, however, is cooperation with other organizations with like interests and objects. To this end, the Geochemical Society has become an Associated Society of the Geological Society of America, a member organization of the American Geological Institute, is represented on the Division of Earth Sciences and the Division of Chemistry and Chemical Technology of the National Research Council, and is affiliated with the American Association for the Advancement of Science.

Also, the Geochemical Society joined with the Commission on Geochemistry of the International Union of Pure and Applied Chemistry, and the geochemical

societies of France and Japan, in sponsoring a symposium on Geochemistry in Paris last July and immediately thereafter a field trip to the Auvergne. At a joint meeting of the Commission on Geochemistry and the Geochemical Society, a committee was appointed to study the matter of relations between the two organizations and to make recommendations as to the manner in which they can work together most effectively. The agreement drawn up by the committee reads in part:

> "It is mutally agreed that it will be desirable for members of the Council of the Geochemical Society to serve as observers, members, or officers of the Commission in order to maintain liaison, prevent duplication of effort, and facilitate cooperation.
>
> "It is suggested that the various national (and local) geochemical societies associate themselves with this program by affiliation with the Geochemical Society."

Implementation of this agreement was initiated immediately by electing an officer of the Geochemical Society as an observer on the Commission. A member of the Commission has become a regional vice-president of the Society and another has been nominated to serve on its Council as vice-president.

The Society was represented officially at the Mexico City meeting of the International Geological Congress in September 1956. Informal discussions with the American Geophysical Union and the American Chemical Society relative to joint technical sessions and symposia have met with favour all around.

From these considerations it is evident that the Society is maintaining contact with all of the principal organizations having an active interest in geochemistry, and through its representatives will be adequately informed of the activities and plans of these groups and will apprise them of ours.

*Functions.* The specific interests and activities of the Geochemical Society as an independent scientific organization can be grouped under three headings: (1) education, (2) publication, and (3) research.

(1) *Education.* The progress in geochemistry over the next several decades will depend largely on the number of schools prepared to give training in geochemistry and on the types of training they provide. Thus far curricula in geochemistry have developed independently in a number of different colleges and universities with little or no attempt at coordination, systematization, or completeness of coverage. Also, the departments of geology and chemistry in most colleges and universities are almost completely out of touch with each other. A committee of the Society is currently studying these problems. The first step, of course, is to obtain as complete data as possible on current courses and training in geochemistry. After the data have been collected and analysed, the Committee and Council may wish to make specific recommendations.

(2) *Publication.* When the Geochemical Society was organized one of the stated premises was that existing journals in the field would be encouraged and supported rather than attempting to establish a new technical journal.

One such journal, *Geochimica et Cosmochimica Acta*, had no society affiliation. By special arrangement with the publishers this publication has become the official journal of the Geochemical Society, with mutual benefit. The journal has gained a substantial number of subscribers and members of the Society may now subscribe at greatly reduced rates. Technical editorial control now rests with the

Society through the three administrative editors who make the final decisions on acceptance of manuscripts for publication and who are all active and interested members of the Society.

An auxiliary publication, *Geochemical News*, has been undertaken to serve as a clearing-house for information about individuals, institutions, meetings, research projects, publications, etc., and is sent to all members of the Society at no additional cost.

(3) *Research.* There are many things that an active and lively society can do to further research without sponsoring and administering projects directly. As with the study of educational problems, the first step is to prepare a survey of what is being done. For this purpose a Research Committee has been appointed. It includes six regional representatives outside of the United States. No attempt is being made to compile a complete catalogue of current geochemical research; rather, information is being sought on new projects and others that are not generally known. Summary reports of the committee will be made available from time to time through *Geochemical News*.

One of the present difficulties in geochemical research is lack of a method for detailed comparison of results from one laboratory with those of another. The only practicable solution is to have available adequate inter-laboratory standards of naturally occurring materials that cover the range of determinations currently being performed in the laboratories concerned. The advantages of this approach have been adequately demonstrated by the interlaboratory comparisons of analyses for both major and minor elements in the granite (G–1) and diabase (W–1) samples distributed by the U.S. Geological Survey. The Committee on Geochemical Standards is studying this problem. The two chief questions it has to answer are "where should the programme be set up and how administered?" and "what materials should constitute the series of standards and what is the best way to get a satisfactory supply of each?"

## Example of Cooperative Research

I do not propose to attempt to catalogue here the geochemical research that should be, or might be, undertaken. I should like, however, to outline for you the impressive results obtained recently by a broad cooperative attack on an important geochemical problem, to suggest other areas in which an analogous attack could solve, or contribute to the solution of major geochemical problems, and to suggest how these broad attacks could be launched in the near future.

At the close of World War II, the United States found itself with an adequate appreciation of the importance of uranium, but with woefully inadequate domestic sources. Two courses were open: (1) to cover the country as completely as possible, looking for any and all types of deposits or (2) to study known deposits thoroughly with a view toward increasing their production significantly and discovering additional similar deposits in the same areas. Under the circumstances it was felt that both possibilities had to be pursued to the fullest, but it is with the results of the second approach that we are now concerned.

### *Colorado plateau uranium deposits*

The Division of Raw Materials of the Atomic Energy Commission, with the

cooperation of the U.S. Geological Survey, the U.S. Bureau of Mines, State geological surveys, university geology and chemistry departments, drilling and mining companies, and numerous other organizations, mounted what was probably the most extensive and intensive study of a type of mineral deposit ever undertaken. This programme has lasted a full 10 years and is just now tapering off significantly. At the height of activity in fiscal year 1954 the A.E.C., other cooperating government agencies, and private contractors employed approximately 650 men in field and laboratory studies of the plateau-type uranium deposits at a total cost of over $8,000,000. This is a tremendous amount of effort to put into studies of one type of deposit, especially one that had produced little more than token amounts of uranium at the time the programme was undertaken. But if it was a gamble, as it was considered by many at the time, it has paid off in jack pot proportions, as we shall see presently, in both material and scientific results.

Studies of these deposits that had been made before the intensive A.E.C. programme got under way had shown that:

(1) The ore occurs predominantly in sandstone.

(2) There is little apparent control by structures such as joints, faults and folds.

(3) There is a close relation, however, between ore and sedimentary features such as sand lenses, channel-fill, cross-bedding, logs and other organic material, etc.

These observations led to the idea that the ore was either deposited during the time the sediments were being laid down or was formed by the action of ground water a comparatively short time thereafter. In either case the ore would be confined entirely to certain stratigraphic zones and there would be no point to looking for richer or more extensive primary deposits at greater depth. Indeed, this philosophy controlled prospecting for many years and an early report recommended specifically that prospecting and development be restricted to these zones. It was also assumed that since the ore had been deposited from ground water it was essentially completely oxidized. Any unoxidized (black) ore, therefore was regarded as a mineralogical curiosity without importance as far as production was concerned.

The A.E.C.–U.S.G.S. group, however, took a broader view of the problem and wanted to make much more detailed studies on source of material and manner of formation of these deposits. To be sure, even if they were syngenetic, or formed later by action of ground water, there were large unexplored areas where extensions of known deposits and similar undiscovered ones could be anticipated. If the metals had been brought up from depth, however, the possibilities expanded in three dimensions instead of two, with the additional chance that some of the underlying primary ores would be richer than the oxidized ores near the surface.

The problem was therefore attacked on a broad front in the following ways, with the result indicated under each:

(1) *Geologic mapping* had been under way before the "crash" programme was initiated and had already provided a great deal of information about the distribution, nature and local controls of the deposits. Throughout the programme geologic mapping has continued to be the principal project, continually turning up new information, suggesting modifications of previous interpretations, furnishing the materials and data for other projects, and in general serving as the focal point for the programme. Data obtained in the laboratory must correlate with

field facts and present a consistent picture before they are useful in making interpretations about the deposits.

(2) *Mineralogy.* Early studies of the plateau ores mention only the highly oxidized minerals such as carnotite, tyuyamunite, pascoite, fervanite, hewettite, and rossite. As more intensive work was undertaken, however, traces of unoxidized minerals such as uraninite and the new minerals coffinite (a uranium silicate) and montroseite (a vanadium oxide) were found in the interiors of some of the larger ore bodies and in stringers and fissures underneath ore, along with sulphides of some accessory metals of the ore (copper, iron, lead and zinc). These primary minerals now constitute the principal reserves on the Plateau.

This mineral assemblage provided the first suggestion that the ore-bearing solutions may have come from depth and may have been at temperatures higher than those corresponding to depths of burial. Subsequent studies of some of the sulphides have indicated formation temperatures of the order of 150°C.

Crystal chemical studies of some of the minerals have been most helpful in unravelling their relations, especially where associations are complex and where previously unknown phases are involved. Indeed, if such studies of the vanadium minerals in these deposits had not been made, their interrelationships might still be a mystery.

(3) *Age determinations and isotope studies.* If the deposits are essentially syngenetic, their primary minerals should show an absolute age approximating that of the enclosing sedimentary rocks. Since the host rocks are mid-Triassic to Upper Jurassic their ages in years should be well over 100,000,000. Repeated determinations on the best (freshest) uraninite available, however, gives ages from 60,000,000 to 75,000,000 years, indicating that the mineralization took place long after the rocks were formed, probably either in the late Cretaceous or early Tertiary.

Studies of the isotopes of lead in galena as well as in uranium minerals from localities all over the Plateau indicate clearly that old radiogenic lead was brought in by the solutions that formed the minerals. This lead must have been derived from an older source, presumably underlying (basement) rocks, because of the difficulty of accumulating old radiogenic lead from the sandstones themselves or from younger intrusive or volcanic rocks.

(4) *Thermodynamic relations.* Fields of stability of the oxides and hydroxides of uranium and vanadium in their various states of oxidation have been calculated as functions of pH and oxidation potential. From these data, diagrams have been constructed showing probable fields of stability for many of the major minerals of the Colorado Plateau. These diagrams are consistent with the picture suggested by the geologic-mineralogical relationships, that is, the deposits were formed at depth in a reducing environment and are being oxidized where atmospheric oxygen reaches them. In general, especially where there is vanadium in the ore, the secondary minerals reflect quite accurately the form and size of the unoxidized ore body, which gives a clear indication that the minerals of these ore bodies have not been moved for significant distances by the action of surface or ground waters.

(5) *The drilling programme* has not only contributed to determining the extent of known ore bodies but has also enabled the geologist to test structural interpretations and other aspects as guides to finding new deposits.

Many other projects, such as geochemical, geophysical, geobotanical, and hydrogeochemical prospecting for uranium, organic geochemistry of uranium, studies of minor elements in uranium deposits, synthesis of uranium-bearing minerals, etc., have contributed a great deal of data leading to better understanding of such problems as nature of ore bearing solutions or original composition of the deposits.

This concerted attack has not only developed a great deal of fundamental knowledge about this type of deposit and geological processes in general, but it has also increased uranium production in the United States manyfold. It is not possible to make a comparison between present production and that at the time this intensive study was undertaken, because figures on tonnages of ore produced during the early years of the programme are still classified. Some idea of the order of magnitude of the increase can be obtained, however, from the fact that production for the period 1 July, 1956, to 1 January 1957 (1,500,000 tons) was more than double that for the same months of the preceeding year (746,000 tons).

*Reserves.* During the ten years this cooperative attack has been under way, in spite of the greatly increased rate of removal of ore, estimated reserves have increased by a factor of almost 50. On 1 July 1947, there were only 1,200,000 tons of 0·18 per cent ore blocked out on the Plateau. On 1 July 1957, there were some 57,000,000 tons of ore averaging 0.28 per cent $U_3O_8$.

*Unexpected dividend.* These results were the direct products of the programme, which were diligently sought after. A perhaps even more impressive indirect result emerged quite unexpectedly from the A.E.C.–Geological Survey uranium studies. Prospecting for uranium in the Blind River area, Ontario, had revealed radioactive anomalies in conglomeratic zones in the Mississagi quartzite, but no uranium was found by chemical tests and the prospecting was abandoned.

Later, however, one of the men who had been concerned in the search happened to read a report of work done by the Survey on the leaching of uranium by $H_2SO_4$, and its application to uranium surveys in areas where $H_2SO_4$ could have been produced by the oxidation of sulphides. It was fairly evident from the outcrop that the radioactive zones in the Mississagi had contained pyrite, from which it was reasoned that the uranium had been leached near the surface where $H_2SO_4$ was produced by oxidation of the pyrite, but that at depth these zones should still be uraniferous. Drilling down dip established that this was indeed the case and a subsequent intensive drilling programme has proved reserves in this one area of approximately 400 miles$^2$ that are greater than the known reserves of all types of uranium ores in the United States combined. (At least 320,000,000 tons of ore averaging 0·1 per cent $U_3O_8$ and possibly as much as 500,000,000 tons.)

## Lateritization

Such spectacular results are not to be anticipated twice in one generation, but the findings on the Colorado Plateau alone amply justify the extension of this kind of approach to other types of deposits and to other kinds of problems where chemistry and related sciences are applied to geology.

Deposits of aluminous and nickeliferous laterite are widespread and no doubt will assume an increasingly important place in the world mineral economy as their distribution, extent, and minor element contents are determined more exactly.

Yet very little is really known about these deposits beyond their mineral and general chemical compositions and the fact they are related to some kind of tropical weathering.

*Studies proposed*

We do not even know for sure whether such deposits are forming under present day tropical conditions or whether tropical weathering is now producing only "lateritic soils" which will never become true laterites with existing climatic conditions. Answering this question should be one of the first aims of a comprehensive study of the laterite problem. A definitive answer will require an attack from several angles, involving at least:

(1) Detailed field work with correlative mineralogical and experimental studies to attempt to demonstrate whether the minerals of bauxites and laterites are actually forming and being concentrated anywhere today. This will be an extensive undertaking, because it will require studies of weathering in areas with all sorts of climates under which lateritic soils appear to be forming, and under which deposits of bauxite and laterite might be produced if current processes are continued long enough.

(2) Detailed geomorphologic studies to demonstrate whether well developed deposits of bauxite and laterite are stable under any existing climate(s), or whether they are everywhere being destroyed.

(3) Absolute age determinations on the most recent of these deposits; relative ages being determined by the studies under (2).

If it is demonstrated that such deposits are not forming now, then the problem becomes an interesting one in paleoclimatology: What *were* the conditions under which they were formed? Temperature can probably be estimated from compositions, including isotope ratios, of some of the characteristic minerals. Other necessary conditions can be approximated by determination of the fields of stability, in terms of Eh, pH, and composition of solutions of the various minerals involved. Comparison of the overlapping fields of stability of the minerals comprising a given deposit will then indicate, within certain limits, the conditions of formation of the deposit, especially if the temperature of formation has been estimated independently.

If it is determined that these deposits are continuing to form, then the requisite conditions can be determined much more directly, but probably no more easily. Lateritization (formation of lateritic soil) is in some respects like the blind men's elephant; one's opinion of it depends on the location and direction of approach. Many factors have been suggested that might influence lateritization, such as amount and seasonal distribution of rainfall, relation to water table, effect of porosity, evaporation from surface of the ground, direct and indirect effect of vegetation, action of iron bacteria, nature of pore solutions and gases, etc.

Some of these have been suggested on purely theoretical grounds; others because certain conditions obtain where laterite exists and a cause-and-effect relationship appears possible. Objective evaluation of these and other possible factors would demand a coordinated study of deposits in enough different places to involve in one or more of the areas all of the factors being considered, e.g. the Caribbean and Pacific Islands, nothern South America, south-east Asia and the Philippines, India, and tropical Africa.

Again, pertinent laboratory studies would be important. In this case (deposits actively forming), studies of rates of transformation and rate of attainment of equilibrium would also be very important. Since the temperatures are low relative to hydrothermal studies the rates are much slower; consequently radioactive tracers could probably be used to advantage in these determinations.

*Ancillary problems*

In the course of these extensive studies attention should be paid to any other information that can be obtained simultaneously. Two such items that have more economic than genetic significance come readily to mind:

(1) *Minor elements.* As much data as possible on the distribution of minor elements in bauxites and laterites should be obtained. Significant amounts of nickel, chromium, cobalt and niobium are known in such deposits in addition to the major constituents aluminium, iron, and in some places, manganese. It is unlikely that a deposit will be worked primarily for one of these minor elements, but recovery of one or more of them might mean a profit from an otherwise unworkable deposit. At any rate, recovery of any of these increasingly hard to get metals would be desirable.

Studies of minor elements might also suggest source of material for certain types of laterites, nature of the original rocks, certain conditions of formation, etc.

(2) *Deposits covered by laterites.* Some areas of laterite or lateritic soils in the tropics blanket thousands of square miles so deeply and completely that prospecting for mineral deposits by the usual means is out of the question. When such an area is undergoing an intensive study attention should be paid to possible means of localizing unexposed ore deposits.

If the composition of such a deposit, either with respect to major or minor elements, is significantly different from that of the overlying material, then a geochemical anomaly might be detectable at the surface above the deposit.

If the appropriate physical properties of an underlying deposit are sufficiently different from those of the cover and from those of the rock(s) in which the deposit is located, then an indication of its presence should be obtainable by the corresponding geophysical determinations—gravimetric or magnetic anomalies, seismic studies, resistivity measurements, etc.

## Mississippi Valley Type Pb–Zn Deposits

*Status of problem*

With the approaching exhaustion of the Mississippi Valley type of lead–zinc deposits and the failure thus far to locate adequate domestic reserves of these metals in other types of deposits, it becomes increasingly important to see whether an intensive and extensive study of source and manner of formation can aid in discovering additional deposits of this kind, either near the known deposits, or in other parts of the mid-continent area.

Again, temperature of formation can be important. In addition to the methods suggested above for laterites, liquid inclusions should provide an independent check. This information, coupled with data on direction of motion of the solution (especially from the deepest parts of the known deposits), should provide a definite

answer to the old problem of source of the solutions; i.e. were they surface water working its way down, ground water flowing laterally, or hydrothermal solutions coming up from a source in depth?

If surface and/or ground waters have formed this type of deposit, there is no point to looking for similar deposits at depth, and little chance that additional ones of any importance will be found near the surface. There are many indications, however, that ascending solutions warmer than ambient surface or near-surface temperatures have been involved in their formation. Preliminary temperature and direction-of-motion studies suggest that this is the case, as does the fact that the deposits consist largely of sulphides, which is not consistent with their deposition by near surface solutions rich in oxygen. Penetration of galena-sphalerite bodies at depth in wells and the widespread occurrence of coals high in zinc indicate that these ascending solutions have been active in many places in the Mississippi and Ohio Valleys where lead–zinc deposits are not currently known.

*Proposed studies*

An intensive study of this type of deposit should begin, of course, with the environs of the best known ones. One of the reasons for suggesting deposition from surface-derived solutions is the absence of regional or local structures that might have served as channelways for ascending solutions. The deposits may have formed at the tops of such structures, however, so evidence for their existence should be sought below the deposits, either by direct observation in the lowest levels reached and drilling therefrom, or at greater depths by geophysical means.

Whether such structures are located or not, evidence for a possible source-rock should be sought and its nature ascertained if possible.

The region involved is so vast and the thicknesses of sedimentary rocks over the basement so great that a geophysical and drilling programme designed specifically to outline promising areas is beyond the realm of reality. So much pertinent information has already been accumulated by oil and coal companies, governmental surveys, and other organizations, however, that if it could all be obtained and plotted on one map, or a series of maps, and supplemented by specially designed studies, areas favourable for more detailed studies or even for prospecting might become apparent. Data plotted on the map should include:

(1) Depths to bedrock.

(2) Bedrock configuration, where local details are available.

(3) Nature of bedrock, where samples have been studied, or can be obtained for study.

(4) Regional and other structures that might serve as, or be related to, channelways for solutions.

(5) Concentrations of zinc, lead and other minor elements in sedimentary materials, particularly coal and limestone.

(6) Areas of dolomitization.

(7) Occurrences of sulphide mineralization.

(8) $C^{12}/C^{13}$ and $O^{16}/O^{18}$ ratios for limestone and dolomite. Very few such determinations will be available, but additional ones should be made, especially from areas indicated as favourable ones by the other factors plotted.

## Granitization

The problem of the origin of rocks of granitic composition has been a major one in petrochemistry for many years. This is a problem of considerable practical as well as theoretical importance, because ore deposits can be genetically related to intrusive granites, but not to metasomatic ones. The fortunes of the battle have moved first in one direction and then in the other; influenced more, one sometimes feels, by oratory and sentiment than by evidence and logic.

Most of the evidence has been from field occurrences, where a very large percentage of the observations can be used to support either point of view, depending on the direction of approach, both physical and intellectual.

Both sides have presented some chemical arguments, but they have been woefully weak for a general solution of the problem. The magmatists have demonstrated repeatedly that rocks of the composition of supposedly granitized sediments *can* be produced by magmatic differentiation, but they have failed to convince the opposition in specific cases that they *were* produced in this manner. The migmatists, on the other hand, have confined their chemical arguments largely to paper calculations showing what elements would have to move in which directions to explain supposed transfers out of and into country rocks to produce the observed rock compositions, but without citing overpowering evidence that such transfers have occurred.

No amount of field evidence is likely to provide general criteria for distinguishing magmatic granites from granitized material. There is a good chance, however, to develop chemical criteria for making the distinction and several lines of research should be pursued with this in mind:

(1) *Temperature determinations* may show characteristic ranges. Magmatic granites certainly have a higher average temperature of formation than do metasomatic ones. If it can be shown that the temperatures of formation do not overlap, then the distinction is clear-cut. If there is overlap the situation will be complicated, but temperature of formation will probably still be useful in many cases.

(2) *Composition of liquid inclusions*, including isotopic constitution of the water, should be different in magmatic minerals from those formed by metasomatic processes. What evidence there is indicates that magmatic water is heavy. We might expect that metasomatic solutions, having diffused for a considerable distance through country rock, might be somewhat lighter.

(3) *Minor elements in minerals.* Especial attention should be paid to groups of related elements. For example, the rare alkalies are likely to show a different concentration and different ratios to potassium present in potassium minerals such as feldspar, biotite, and muscovite in the two types of rocks. Such studies are just getting under way and preliminary results indicate that rubidium shows higher than "normal" Rb/K ratios only in the end products or near end products of magmatic differentiation. Similar studies should be made for the alkaline earths, selected heavy metals, etc.

## Meteorites

### *Geologic possibilities*

Perhaps the chemistry of meteorites is not strictly geochemistry, but these bodies from outer space have been pelting our planet so long and so vigorously

that we should be able to use their chemical and mineralogical characteristics to help solve some problems of earth history.

It is commonly assumed now that meteorites were very much more numerous during the early stages of the earth's history than they are now. If this is true they were either "burned up" completely as they came into the earth's atmosphere, or weathered completely, because meteorites are unknown in the stratigraphic column. In either case their substance would have been added to the sediments then being laid down and we should be able to find some indication of this process in the sedimentary rocks, particularly the shales.

The outstanding chemical characteristic of the metallic phase of meteorites is the high content of nickel. Siderites and the metallic phase of stony meteorites contain many times as much nickel per gramme of iron as do the common ferromagnesian minerals the weathering of which has supplied most of the terrestrial iron (and nickel) of the sedimentary rocks.

If meteorites were significantly more abundant in the geologic past, then sedimentary rocks of a given type should increase in nickel content and in their Ni/Fe ratio with increasing age, and with sufficient data it should be possible to compare the rate of accretion of early geological times with the present rate. Then, assuming a straight line decrease, the total amount of meteoritic material added since the formation of the earliest preserved sedimentary rocks could be estimated.

There is still uncertainty as to whether SiC (moissanite) occurs in meteorites. If it does, then it should also be found in increasing amounts in old clastic rocks. This could provide a check on the results of the studies of nickel in sedimentary rocks, but the determinations would be much more difficult and time consuming.

*Tektites*

Chemistry can also contribute to the solution of problems of meteorites as such. One of the most fascinating of these is the origin of tektites, which has been a puzzle ever since moldavites were first described in 1787. It is now generally agreed that they are extra-terrestrial in origin, but the great gap between their chemical composition and that of the stony meteorites closest to them in make-up is still unexplained.

There is little doubt that the iron and stony meteorites came from the break-up of a planet of the same general size as the terrestrial planets. In other words, the body was large enough so that differentiation must have taken place as it cooled and solidified. Also, it was large enough to hold an atmosphere. Iron meteorites are easily explained as having come from the core of such a body; stony meteorites of various compositions, from the various layers of the partially differentiated mantle.

But what of the tektites? If they were the product of extreme differentiation there should be a whole series with intermediate compositions; not a single one has been reported. Moreover, tektites do not have the composition of any igneous rocks; rather, they are more like high silica–alumina shales in composition.

It is logical to suppose that the parent planet of the meteorites had a thin crust that was somewhat more highly differentiated than the mantle that produced the stony meteorites. It is not necessary to assume much further differentiation of the

crust; just a slightly larger percentage of the components of feldspar than stony meteorites contain, with potassium feldspar approximately equal to the sodium feldspar, can explain tektite compositions as the result of weathering. The overall composition would differ very slightly from that of the silicate fraction of the average stony meteorite.

If the atmosphere of our Astropher consisted predominantly of water with enough of a mineral acid (HCl or $H_2SO_4$) to produce a pH that would prevent the precipitation of the hydroxides of iron and magnesium as well as their carbonates (if $CO_2$ was present), then a simple weathering process would decompose the olivine and pyroxene, and remove practically all the iron and magnesium to the oceans, and leave most of the silica behind as an insoluble residue. The feldspars would alter to minerals like sericite, paragonite, clays, etc., retaining essentially all of the silica, alumina, lime, and alkalies in solid phases, which would either form a residual blanket or sedimentary layers in the seas.

In either case, when the body disintegrated the oceans would be vaporized and their contents of iron, magnesium, and any other dissolved salts would be atomized into space and the solid residue from weathering when melted would have a composition well within the range reported for tektites. There is an age discrepancy between tektites and stony and iron meteorites that would require tektites to come from a planet different from the one(s) giving rise to the meteorites whose ages have thus far been determined.

The principal problem of the tektites, then, is to find some characteristic by which it can be proven whether they are of terrestrial or extra-terrestrial origin. A preliminary study seems to reveal sufficient radioactivity induced by cosmic radiation ($Be^{10}$ and $Al^{26}$) to demonstrate an extra-terrestrial origin. However, the uncertainties in the determinations, both for tektites and for rocks that have probably lain on the earth's surface for a comparable length of time, are such that the interpretation is not yet definite.

This work should be continued and refined, both on tektites from various localities, and on better rock samples than have been available thus far. Also, other criteria should be sought, such as amount and isotopic composition of water in tektites and in the glassy portion and hydrous minerals of stony meteorites, assemblages and amounts of trace elements in tektites, and more definitive interpretations of their textures and primary and secondary structures.

## Geochemistry of Petroleum

### *Need for geochemical studies*

The oil companies have realized for some time that in intensively prospected areas like the mid-continent and gulf coast regions geophysical methods have located practically all of the structures that can be found this way and that there must be increasing dependence on geochemical methods, not only direct geochemical prospecting, but also broader studies of the geochemistry of petroleum and its origin.

Studies are now beginning with the organic geochemistry of modern sediments in an attempt to identify and characterize original source materials. This information, together with an evaluation of factors responsible for conversion of the

organic materials to petroleum such as temperature, pressure, shearing, radiation, biological processes, etc., can give new ideas concerning types of sediments and environments that favour formation of petroleum. These ideas should prove useful as supplements to geophysical determinations of structure and geochemical patterns, especially in young sedimentary rocks such as those off-shore along the Gulf coast.

The evaluation of the factors mentioned above must be done partly in the laboratory and partly by field studies. Experimental determination of conditions and rates of transformation of probable source materials to petroleum or to petroleum-like substances can be suggestive, but must be checked against actual occurrences before valid interpretations can be made.

*Prospecting possibilities*

Geochemical prospecting or just "geochemistry" still means to a great many people in the petroleum industry the first kind of geochemical prospecting that was done in searching for petroleum—looking for haloes of hydrocarbons in the soil above oil-bearing structures. This method quickly fell into disrepute when it failed to correlate surface patterns of hydrocarbons with deposits of these compounds in the underlying rocks. It was given up almost entirely when it was demonstrated that so much of the hydrocarbon content of soils is from the decomposition of modern organic materials that it was not possible to identify any part of it that may have escaped from oil pools.

$C^{14}$ *in hydrocarbons.* Times and techniques have changed since the 1930's, however, and it may not be inappropriate to suggest that another look should be taken at this and related methods of prospecting. Since it was abandoned, the discovery of carbon-14 has made possible the positive distinction between modern and ancient carbon-containing compounds. Hydrocarbons derived from modern organic substances have practically the equilibrium amount of carbon-14; those from petroleum are dead with respect to radioactivity. By counting a sample of methane, for example, it should be possible to say whether it is all modern, or to determine the percentage of old gas in a given sample. Then plotting the distribution of the inactive fraction only might reveal haloes or other significant patterns above accumulations of oil.

*Trace elements.* It is well known that various crudes contain easily determinable amounts of characteristic trace elements and it has been suggested that their concentrations may be dependent upon the paleogeography of the time when the containing sediments were laid down. If the overlying rocks and the soils are low in the trace elements concerned, and if the compounds containing them can escape from the oil-containing structure, then a surface distribution pattern for one or more heavy metals from a reservoir might reveal its presence.

*Radioactivity.* It has been suggested that radioactive anomalies at the surface indicate oil pools underneath. Since radon is the only radioactive element that is likely to move outward from such deposits, however, and since its half-life is less than 4 days it is difficult to say what would produce the supposed anomalies.

*Isotope ratios.* Studies of the isotopic constitution of compounds migrating away from oil accumulations offer a fruitful field for prospecting. There are

indications that the $N^{14}/N^{15}$ ratio increases away from the centre of a field, and that the $S^{32}/S^{34}$ ratio of $H_2S$ increases with increasing distance above oil-bearing horizons. These determinations should be checked and similar studies made of other gases, particularly helium and the lighter hydrocarbons.

## Geochemistry of Natural Waters

Water has very commonly been taken for granted in the past. Industry, agriculture, and other users of large quantities of water have gone where sufficient quantities of the requisite purity were available without asking why the water was where it was, or had the necessary properties, or whether the supply would last. So many of these ventures have now come to grief, or have at least been placed in a very precarious situation because of the changing quantity or quality of their water supplies, that it is becoming increasingly important to answer some of these "how" and "why" questions of hydrology. The importance of such studies has recently been underlined by the establishment and implementation of a national water policy correlative with that for minerals.

To be sure, water supply has been correlated with physical factors such as amount of precipitation, drainage areas, structure, evaporation, etc., but very little attempt has been made to evaluate the geochemical factors influencing water supply.

### *Ground water*

The geochemistry of ground water centres around the relationship between the chemistry of such water and the character of the containing formations. It is known, for example, that certain aquifers soften water at depth by a base exchange between the calcium bicarbonate of the near surface water and the clays or clay-like minerals of the aquifer. Yet no attempt has been made to determine how much clay mineral is required to soften a sec-ft of water, how much effective base exchange capacity the aquifer has (i.e. how much active clay-mineral it contains), rate of base exchange, volume of the aquifer supplying the wells of a given area, rate of flow in the aquifer, etc., from which it would be possible to estimate the life of the wells for producing water of a given quality.

These studies should be divided into two categories:

(1) A study of the general relationship between type of formation and character of ground water.

(2) Detailed studies of individual formations and the waters they produce.

### *Surface water*

Similar studies should be made of the waters of streams. Belatedly, arrangements are being made for I.G.Y. parties to sample some seventy-five principal streams of the world above tidewater, but near their mouths, from one to four times during the year. The resulting analyses will give valuable integrated data on total runoff and amounts of dissolved solids contributed to the sea annually, but will add very little to our knowledge of the geochemistry of any individual stream.

It would be impossible to undertake detailed studies of all of these principal streams in the near future, but pilot studies should be made on at least one entire

basin of a major stream. The basin should be divided into areas that are essentially homogeneous with respect to the factors considered. Thus it would be possible to evaluate not only the effect of natural factors such as geologic units present, stage of erosion, degree of weathering, soil cover, vegetation, etc., but also the result of artificial aberrations such as density of population of people and domestic animals, types of communities (including methods of sewage disposal), contamination by mines, mills and other types of industrial establishments, etc.

Some studies of single factors have been undertaken on individual streams, but no attempt to study a major stream basin exhaustively has been made. Such a comprehensive study would have many advantages beyond improving our knowledge of the quantity and quality of water obtainable from the river system. For example, abnormal amounts of metals, not related to mines or other sources of artificial contamination could indicate favourable areas for prospecting. Results of such a study could be very helpful in planning and executing pollution control programmes. Principles developed should allow prediction of types of water in an undeveloped basin just from a general knowledge of its geology and soil types. Behaviour of elements related to those of radioactive wastes should delineate favourable areas for disposal of low-level waste.

*Chemical oceanography*

There are innumerable problems, of course, in chemical oceanography that require more work and that would profit immensely by a cooperative attack. Development of new techniques involving isotope studies, however, especially radioactive hydrogen and carbon, tend to emphasize studies involving massive movements of material in the atmosphere and hydrosphere and exchanges of material and establishment of equilibrium between these two spheres. It is particularly important that worldwide synoptic studies involving $H^3$ and $C^{14}$ be undertaken as soon as possible and continued indefinitely, because of the significant increases of tritium concentration produced by explosions of H-bombs and the apparent relative decrease of $C^{14}$ in atmospheric $CO_2$ because of the addition of immense quantities of "dead" $CO_2$ from modern industry.

If, as appears to be the case, significant quantities of tritium have not yet penetrated the southern hemisphere, detailed studies of representative areas should be made before such penetration occurs for the purpose of establishing "normal" pre-H-bomb patterns for various types of climate and terrain. These would be of considerable interest and help in interpreting present patterns in the northern hemisphere. Continuing studies, with particular attention to distribution before and after H-bomb blasts, should yield much information on hemisphere-wide movements of air masses.

Detailed and continuing synoptic determinations of the amount and activity of $CO_2$ in the atmosphere and in water at widely scattered localities can be invaluable in providing at least partial answers to such far reaching problems as:

(1) Is modern industry increasing the $CO_2$ content of the atmosphere measurably?

(2) If so, what effect is this having on the earth's climate?

(3) What corrections must be made for $C^{14}$ ages to allow for this factor?

(4) What is the influence of the ocean in regulating the $CO_2$ content of the air?

(5) How long a time is required for establishing $CO_2$-equilibrium between the ocean and the atmosphere?

(6) What is the "turnover" time for various oceans?

(7) What is the scale of the convection cells, equator to poles, or are they more localized at least in some cases?

(8) Are there ocean deeps that are not involved in this turnover, hence essentially cut off permanently from the surface?

(9) Are any of the major ocean currents changing at an observable rate?

(10) What are the details of hemisphere-wide and world-wide oceanic and atmospheric currents? Determinations of substance other than $CO_2$, such as $H^3$, Na, Cl, $SO_2$, $SO_4$, etc., in the air and in rain samples could be very helpful in depicting the atmospheric movement picture.

Answers to these questions are of prime importance to all aspects of meteorology, of course, but have other significant connotations in such diverse fields as disposal of high level radioactive waste, theoretical rate of food supply possible from the oceans, biological oceanography, and military and commercial aviation. Some plans are under way for $CO_2$-sampling during the I.G.Y. which may provide answers, or partial answers, to some of the above questions.

*Radioactive isotopes.* Studies of $H^3$ and $C^{14}$, along with the stable isotopes of these same elements and those of oxygen, have been used in a variety of problems in meteorology and hydrology, but should be extended to new types of problems, or to refinements of those already undertaken.

For example, very little is known about the rate of movement of ground water except in isolated cases where rate of flow has been determined over short distances between two wells in a shallow aquifer. It would be much more important to determine the average rate of flow in an aquifer outcropping along the Rocky Mountain front and carrying water to plains communities up to hundreds of miles away.

This might be possible, if $H^3$ and/or $C^{14}$ are used as radioactive "tracers". If we know the concentration of tracer in the water going into the aquifer then, knowing its half-life and assuming that none has been added or subtracted in transit, if we can determine the concentration at any point down dip we can calculate the "age" of the water at that point. Then dividing the age by the distance from the intake area gives the time required for the water to travel a unit of distance.

The assumption that no tracer is added in transit is no doubt justified, but that none is subtracted is quite another matter. The $CO_2$ in the water may exchange with the calcium carbonate in the aquifer. Likewise, water molecules containing $^3H$ may exchange, even preferentially, with water of crystallization of hydrous phases, or $H^3{}_2O$ may be adsorbed preferentially on clays and similar minerals. Evaluation of these factors must precede any attempts to use these methods for accurate estimates of rate of motion of waters through aquifers.

*Juvenile water.* H/D and $O^{16}/O^{18}$ studies have been used in a variety of problems in meteorology and hydrology. One of the most interesting of these is the attempt to estimate the amount of magmatic water in hot springs and geysers. It would appear, however, to be more logical to attempt to characterize juvenile water

by studying the earliest hydrous magmatic fractions rather than taking water expelled from the last fraction to crystallize, and that so near the surface that the magma may have absorbed some ground water in the course of its ascent. Mix these uncertain exhalations with an indefinite amount of near-surface ground water and the problem becomes complicated indeed. If we start at the other end of the scale, however, and study the water from the earliest and most deep seated magmatic fractions available, there should be a minimum of contamination with surface water and consequently a closer approximation to the isotopic composition of the original water.

Perhaps one of the best materials to start with would be the serpentine of a deep-seated and uniformly, but not completely, serpentinized dunite or periodotite. The geologic evidence is that such a body has retained its original water to react with olivine when the temperature is low enough.

Another approach would be to determine the isotopic composition of water from successive fractions from an intermediate igneous rock. For example, fresh material is available in canyons to a considerable depth in the Sierra Nevada batholith. Study of water samples derived from hornblende, biotite, chlorite, liquid inclusions in feldspar and quartz, and water of the intergranular spaces should be very interesting and instructive. The sequence could be extended by studying hydrous minerals and liquid inclusions in pegmatites and aplites in the granodiorite and in associated veins, such as those of Grass Valley, California. If the water shows a progressive change in isotopic composition from early to late fractions the data may provide a scale for estimating the stage of crystallization reached when a given phase separates. At any rate, the weighted average of all of the fractions should approximate the isotopic composition of the original water of the magma.

## International Geochemical Year

### *International cooperation needed*

Most of these problems can be attacked, as some of them have been in the past, piecemeal—with piecemeal results. But for answers of general significance, for results that will not have to be revised when the next partial study has been reported, for rapid advances in knowledge, a broad coordinated approach is called for; broad subject-wise in utilizing all pertinent disciplines and approaches; geographically, in selecting a complete range of types of deposits, conditions, phenomena, etc.

*Field work.* In studies of lateritization, for example, no one locality, nor, indeed, any single country, has all of the climatic conditions that have been cited as characteristic of lateritic weathering. Conclusions that appear inescapable in Jamaica may be inadmissible in East Africa or India. As may different situations as possible should be studied simultaneously and the results integrated completely. This will require a high degree of international coordination and cooperation.

Hydrothermal processes and the nature of the ore forming fluids are the same in Kazakhstan or Winnemucca and the closer we keep in touch with work in these fields abroad, the more rapidly will our knowledge of them increase.

*Dissemination of knowledge.* The finding and distribution of petroleum is a worldwide problem and should be treated as such, yet a number of Russian books

have appeared in the last few years on the accumulation and transformation of organic materials in marine sediments, geochemistry of petroleum, geochemical prospecting for petroleum, the geological implications of bacterial action, dolomitization, colloids in the earth's crust, and other subjects of interest to the geology and geochemistry of petroleum to which little or no attention has been paid in the West. We are busy duplicating much of this work; translation and distribution of these books would render this duplication unnecessary and free our research workers for other needed work. Then, if we could keep in touch with the Soviet workers in these fields this situation need not arise again.

If primary publications as well as informative abstracts of work in the earth sciences can be made freely available on a worldwide basis then, even with no great increase in the amount of effort going into research in these fields, progress will be much smoother and more rapid.

*Exchanging samples and information.* In problems of the chemistry of the atmosphere and hydrosphere, for many of which synoptic sampling and observations are required, international cooperation in collecting and exchanging samples and mutual provision of data is a must. A start in this direction is being made during the I.G.Y., largely not as an integral part of the programme, but as a service to other organizations.

*International Geochemical Year.* What we need is a programme comparable to I.G.Y. to foster international research across the board in the broad problems of geochemistry. A great deal of planning and effort would be necessary, of course, but if the International Council of Scientific Unions, the International Geological Congress, and all interested national societies, laboratories, and institutions could work together in planning an International Geochemical Year to be held five to ten years hence, this rapidly growing science should spring into bloom and produce fruits that would be of inestimable value to man for generations to come.

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# Relative mobility of the common elements in weathering of some schist and granite areas

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**Abstract**—Chemical analyses were made of stream waters and rocks from three local drainage basins within which the rocks are chemically homogeneous. The relative mobility of each major element was computed as the ratio of its content in the mineral residue of the stream water to its content in the rock drained by the stream. The order of mobility in each case was Mg > Ca > Na > K > Si > Al = Fe. This differs somewhat from published estimates based on the composition of average fresh waters and rocks, in which the reported order of mobility was Ca > Na > Mg > K > Si > Al = Fe.

## Introduction

The relative mobility of an element in the cycle of weathering may be defined as the comparative rate at which it moves from its source in the parent rock to the stable environment of a sedimentary basin.

Mobility, defined in this way, is the resultant of many different factors. Some primary minerals, such as quartz and zircon, are resistant to chemical attack, and move relatively slowly as detrital fragments. Others, such as the ferromagnesian minerals and feldspars, decompose fairly rapidly, but yield products that generally are precipitated near the site of weathering as clay minerals and secondary oxides. Some of the decomposition products of the less stable minerals, however, do not take part in the formation of secondary minerals, and tend to move rapidly from the site of weathering in ground and surface waters. In addition to these processes, many other factors affect the mobility of the various elements, such as contact of solutions with adsorptive media, reactions resulting from changes in pH and oxidation potential of the environment, uptake by living organisms, and chemical reactions with organic matter.

A quantitative computation of mobility based strictly on theoretical considerations, therefore, is hardly feasible because of the large number of unknown variables. At the same time, some kind of dependable estimate of the relative rates at which the common elements move in the surficial environment is needed in any consideration of the geochemistry of weathering and sedimentation.

Empirical estimates of the relative mobility of elements have been attempted by various writers, chiefly in two ways.

One approach involves comparisons between unweathered rock and its weathered equivalent. Butler (1953), for example, found that, in the weathering of Cornish rocks, $Fe^{+3}$ was enriched and Si, $Fe^{+2}$, Mn, and Na were impoverished relative to alumina.

The second approach considers the composition of the unweathered rock relative to the composition of the mineral content of the surface waters that carry

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away the weathering products. The present paper is concerned with an appraisal of published estimates of mobility based on analysis of surface water, and presents some new data collected under more controlled conditions.

## Previous Work

Most of the published work on empirical estimates of the mobility of elements by comparisons of the composition of fresh-water residues with that of the parent rocks have been of a general nature, in which average compositions of rocks over wide areas are compared with average compositions of waters over similarly wide areas.

The principal contributors in this field are Smyth (1913) and Polynov (1937). Smyth's estimate applies to the surface of the earth as a whole, whereas, Polynov's estimate applies to igneous rock areas in general.

### *Smyth's general estimate*

Smyth has considered, as a unit, the total mass of crustal rocks acted upon by rain waters. He calculated an order of mobility for the common rock-forming elements by taking the overall average composition of crustal rocks and comparing it with the overall average composition of water residues.

In his calculations, Smyth used Clarke's (1904) estimate for the average composition of crustal rocks. Clarke's estimate represents the average composition of a shell 10 miles thick, of which probably 95 per cent consists of igneous rocks. Since drainage waters act on surface rocks that are 75 per cent sedimentary, it was necessary to take this into account in arriving at a reasonable approximation for the composition of surface rocks. Smyth, therefore, combined sedimentary with igneous rocks in the ratio of three to one to obtain his approximation. The weighted averages for the content only of the seven principal rock-forming elements in crustal rocks, together with the content of the same seven elements in the residues from average river waters, were recalculated to 100 per cent, as shown in Table 1, Column I. Smyth computed the relative "solubility", or mobility, of each element by dividing the content of that element in water residues by the content of the same element in crustal rocks. This procedure is followed throughout the present discussion in order that the relative mobilities, as calculated by the different investigators, may be readily compared.

Thus the figures in Column I give some indication of the relative rates at which the various elements travel in the surficial environment. If Smyth's data and assumptions are accurate, it follows that: Ca and Na appear to move at roughly the same rate; Mg at about one-third this rate; K at about one-eighth this rate; Si at about one-thirtieth this rate; and Al and Fe together, at about one-fortieth this rate.

### *Polynov's general estimate*

Polynov has considered, as a unit, the total mass of surface igneous rocks acted upon by rain waters. His order of mobility was calculated by taking the overall average composition of igneous rocks and comparing it with the average composition of water residues draining areas of igneous rocks.

In his calculations, Polynov used Fersman's (1922) average for the composition of igneous rocks. The average composition of water residues was obtained from Clarke (1924) and represents the average of thirty analyses of waters believed to drain only igneous areas. These averages, recalculated to 100 per cent, together with Polynov's estimate of the relative mobility of the common rock-forming elements, are given in Column II of Table 1.

Table 1. Data for estimates of relative mobility of common elements in weathering

| | | General estimates Smyth (1913) Polynov (1937) | | | | Estimates for specific rocks Anderson and Hawkes | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | I Earth's crust | | II Igneous rocks | | III Littleton schist | | IV Oliverian granite | | V Black Mountain granite | |
| | | (%)* | Ratio W/R | (%)* | Ratio W/R | (%)* | Ratio W/R | (%)* | Ratio W/R | (%)* | Ratio W/R |
| Ca | Water | 52·48 | 6·80 | 36·52 | 5·29 | 25·37 | 5·55 | 42·64 | 18·07 | 27·61 | 12·84 |
| | Rock | 7·72 | | 6·91 | | 4·57 | | 2·36 | | 2·15 | |
| Na | Water | 16·43 | 6·44 | 23·61 | 4·13 | 11·30 | 4·85 | 17·35 | 4·29 | 22·33 | 5·67 |
| | Rock | 2·55 | | 5·71 | | 2·33 | | 4·05 | | 3·94 | |
| Mg | Water | 8·74 | 2·47 | 12·18 | 3·02 | 29·44 | 15·41 | 15·09 | 35·92 | 12·80 | 49·22 |
| | Rock | 3·54 | | 4·03 | | 1·91 | | 0·42 | | 0·26 | |
| K | Water | 3·90 | 0·81 | 10·94 | 2·22 | 7·44 | 0·88 | 3·03 | 0·59 | 3·19 | 0·53 |
| | Rock | 4·82 | | 4·94 | | 8·45 | | 5·11 | | 6·05 | |
| Si | Water | 13·99 | 0·25 | 14·86 | 0·28 | 23·99 | 0·37 | 21·49 | 0·29 | 32·62 | 0·45 |
| | Rock | 56·36 | | 53·04 | | 65·14 | | 73·32 | | 72·28 | |
| Al | Water | 4·46† | 0·18† | 1·19 | 0·08 | 2·07 | 0·18 | 0·14 | 0·01 | 1·20 | 0·09 |
| | Rock | 25·01† | | 15·60 | | 11·32 | | 12·12 | | 13·25 | |
| Fe | Water | | | 0·70 | 0·07 | 0·39 | 0·06 | 0·26 | 0·10 | 0·25 | 0·12 |
| | Rock | | | 9·77 | | 6·28 | | 2·62 | | 2·07 | |
| Total | Water | 100·00 | 1·00 | 100·00 | 1·00 | 100·00 | 1·00 | 100·00 | 1·00 | 100·00 | 1·00 |
| | Rock | 100·00 | | 100·00 | | 100·00 | | 100·00 | | 100·00 | |

* Recalculated to 100 per cent, values given for water are percentages in the solid residues.
† Includes Fe.

The similarity between Polynov's and Smyth's figures is striking. Both the order and magnitude are roughly the same. One notable exception is the relative decrease in the mobility of K in areas of sedimentary rocks. This may be an expression of the greater resistance to weathering of the K-bearing clay minerals in sedimentary rocks as compared with K-bearing minerals in igneous rocks.

*Discussion of Smyth's and Polynov's general estimates*

By comparing the composition of the river-water residues with the composition of rocks that are assumed to occur in the drainage basins of those rivers, as done by Smyth and Polynov, a general estimate of the relative mobility can be calculated. Whether these estimates are valid or not depends, to a large extent, on the assumptions by both investigators as to the composition of the rocks of the drainage basins.

Smyth, in his estimate of the composition of surface rocks, combines sedimentary with igneous rocks in the ratio of three to one. Limestones, dolomites, sandstones, and shales are the predominant rock types included under the classification of sedimentary rocks. The proportions of each of these rock types used in computing an average composition for the sedimentary rocks is of critical importance.

Suppose, for example, that in calculating the average composition of sedimentary rocks, the relative proportion of the carbonate rocks is underestimated. Such an error would decrease the value of the term in the denominator of the ratio:

$$\frac{\%\text{ of element in water}}{\%\text{ of element in rock}} = \text{relative mobility}$$

and indicate a high relative mobility for Ca and Mg. This erroneously high relative mobility would be further enhanced by the greater solubility of the carbonate minerals of limestones and dolomites as compared with other rock-forming minerals.

The proper weighting for the different rock types is equally important in Polynov's estimate for areas underlain by igneous rocks. The average composition of igneous rocks represents the weighted average of felsic and mafic rocks which have different chemical compositions and, to a varying degree, different solubilities. Therefore, errors in the values for relative mobilities could result from improper weighting of these different igneous rock types.

A consideration of the above assumptions, plus the assumption that the stream waters used in the computations do actually drain areas in which the rocks have the compositions stated, suggests that Smyth's and Polynov's estimates of the relative mobilities express only a general relationship. In order to avoid the assumptions used by these authors, it seemed desirable to calculate the relative mobility of the elements for a specific local area, where the composition of both the rocks and the water draining these rocks could be determined more accurately. It was with this thought in mind that the present work was carried out in three local areas of New England.

## Present Work

It follows from the work of Smyth and Polynov that a specific estimate of the relative mobility can be obtained by comparing the composition of the rock in one local area with the composition of the water residues from this area. With this in mind, the senior author sampled waters and rocks in three areas in northern New England (Fig. 1). In the areas selected the geology is well known and the rocks, at least in the drainage basins sampled, appeared to be homogeneous.

Also, the areas combined high relief with a minimum of glacial overburden. For those readers not familiar with the New England climate, the areas are located in the temperate climatic zone and have a normal annual precipitation of between 35 and 45 in.

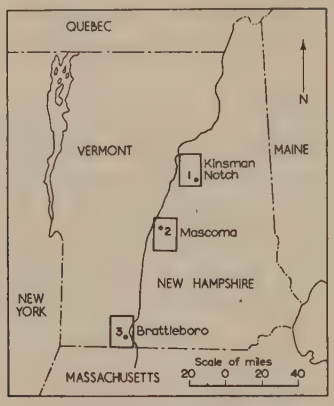


Fig. 1. Sketch map of area in New England showing sample localities.

*Experimental areas*

*Sample locality* 1: *Littleton Schist, Kinsman Notch, New Hampshire.* Water samples were collected from Beaver Brook, which drains the north-east slope of Mt. Blue (el. ±4530 ft) about ¾ mile west of Kinsman Notch, New Hampshire. According to Billings (1937), the rocks of this area consist of mica schist, quartz–mica–schist, garnet schist, staurolite–sillimanite schist and sillimanite schist. Fresh rock samples were taken along the brook for a considerable distance and, although there appear to be many different rock types involved, this method of sampling and the chemical similarity of the members of the metamorphic rock sequence would tend to cancel this apparent inhomogeneity.

*Sample locality* 2: *Oliverian Granite, Mascoma, New Hampshire.* Water samples were collected from a small stream located on the east slope of Moose Mountain (el. ±2000 ft) about ¼ mile north of Gross Neighborhood School, New Hampshire. According to Chapman (1939), the overall composition of this group of rocks ranges from quartz diorite to granite. Major minerals are quartz, microcline, oligoclase, and biotite. Minor accessories are muscovite, epidote, sphene, magnetite, zircon, apatite, and sericite. The rocks from around Gross Neighborhood School are consistently pink granites, so that the requirement of rock homogeneity is apparently satisfied.

*Sample locality* 3: *Black Mountain Granite, Brattleboro, Vermont.* Water samples were collected from a small spring entering the abandoned Presbrey–Leland Company Quarry. The quarry is located on the west slope of Black Mountain (el. ±1300 ft) about 5½ miles north-east of Brattleboro, Vermont. The rock type, according to Church (1937), is a leucogranodiorite. Major minerals are quartz, microcline, albite–oligoclase, muscovite, and biotite. Minor accessories are orthoclase, magnetite, garnet, and epidote. With regard to the uniformity of the rock, Church says: "Plot of traverses showed a high degree of uniformity throughout

the entire area except for a slightly higher percentage of biotite in the southern part of the igneous mass."

*Sampling procedure*

Chip samples of relatively fresh rock were taken for some distance upstream from where the water samples were collected. Water samples of from 6 to 8 l. were collected near the base of the slope and stored in polyethylene containers. Temperature and pH were measured at the time of collection. Table 2 summarizes the data obtained for temperature, pH, and salinity of the water samples.

Table 2. Location, temperature, pH, and salinity of water samples

| Location | Temperature (°C) | pH | Salinity (mg/l.) |
|---|---|---|---|
| Kinsman Notch, N.H. | 2·0 | 5·4 | 10·9 |
| Mascoma, N.H. | 6·0 | 6·1 | 20·6 |
| Brattleboro, Vt. | 9·0 | 5·6 | 15·2 |

*Analytical methods*

A combination of wet chemical and flame photometric methods was used to determine the concentrations of the various elements in the stream waters. The methods used were those recommended by *Standard Methods for the Examination of Water, Sewage, and Industrial Wastes* (1955). The mutual standard method, as outlined by DENNEN and FOWLER (1955), was used in the analysis of the rock samples.

*Specific estimates of the relative mobility*

The figures for the concentration of the various elements in the water residues and rocks, recalculated to 100 per cent, and the relative mobilities of the elements in the areas sampled, are shown in Table 1, Columns III, IV, and V.

The order of mobility for the common rock-forming elements is apparently the same for areas containing a schist, a granite, and a leucogranodiorite. The magnitude varies slightly, particularly with regard to the most mobile elements—Ca and Mg. The question arises as to whether or not this order of mobility is unique for this one particular local area in New England. The answer to this question would be found in more specific estimates similar to the ones in this paper.

*Possible sources of error*

The figures for specific estimates of mobility contain some elements of uncertainty that are extremely difficult to appraise without a considerably more comprehensive study. Some of these sources of error are inherent in the field problem, and some are involved in the treatment of the samples. They may be summarized as follows:

(1) The samples of the rocks may not have been fully representative, even though they appeared to be homogeneous.

(2) Products of weathering of glacial overburden may distort the composition of the stream water. The areas selected, however, were covered by only a relatively small amount of glacially-transported material. Moreover, glaciation helped the study by sweeping away old soils and leaving fresh rock at the surface.

(3) No allowance was made for salt derived from ocean spray and carried inland on air currents. In future work, this correction could possibly be computed from determinations of the chloride content of the stream water.

## Summary and Conclusions

General estimates of the order of mobility of the common elements in the weathering cycle were computed by Smyth and Polynov as follows:

$$\text{Ca} > \text{Na} > \text{Mg} > \text{K} > \text{Si} > \text{Al} = \text{Fe}$$

These estimates were derived from the ratios of the average content of each element in the residues of a large number of river waters, to the average content of that element in a large number of rock samples. The averages of the rock analysis were weighted according to reasonable assumptions as to the relative amounts of the different rock types occurring in the drainage basins of the rivers and contributing weathering products to those rivers.

In the present study, similar ratios were derived from analyses of waters and rocks from three individual local drainage basins within which the rocks are relatively homogeneous chemically. The order of mobility found was as follows:

$$\text{Mg} > \text{Ca} > \text{Na} > \text{K} > \text{Si} > \text{Al} = \text{Fe}$$

The order of mobility as shown by the two studies is the same, with the exception of magnesium, which appears as the most mobile element in the specific estimates instead of third in the sequence as in general estimates. Inasmuch as the uncertainties as to the composition of the parent rocks have been largely eliminated in the specific studies described above, the evidence favours a higher mobility for magnesium in temperate weathering than was previously thought.

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# Parallelisierung von Leithorizonten im Ruhrkarbon mit Hilfe des Bor-Gehaltes

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**Abstract**—Carboniferous pelitic sediments of the Ruhr district are characterized by contents in boron varying with the degree of salinity of the water in which the sediments were deposited. Freshwater sediments have contents in $B_2O_3$ varying between 0·005 and 0·015 per cent; typical marine sediments have contents from 0·03 to 0·06 per cent. These contents seem to be stable during diagenesis and weathering; with incipient metamorphosis they seem to become diminished.

Determinations of boron contents seem to offer possibilities for correlation in non-fossiliferous sequences of changes in salinity, as well as a means for diagnosis of the environment of non-fossiliferous sediments.

## 1. Einleitung

Landergren (1945) hat einen linearen Zusammenhang zwischen dem Salzgehalt des Wassers im Ablagerungsgebiet und dem Borgehalt der Ablagerungen festgestellt. Die Annahme von Goldschmidt (1954), dass der Borgehalt mariner Ablagerungen einen Gang abhängig vom Alter der Ablagerungen zeigt, hat sich nicht bestätigt. Vom Kambrium bis heute ergaben sich im Wesentlichen die gleichen Verhältnisse. Die Borgehalte praekambrischer Ablagerungen lassen vermuten, dass dieselben Verhältnisse herrschten, soweit wir Sedimentgesteine überblicken (Sahama, 1945). Allerdings kann sich der Borgehalt bei der Metamorphose verschieben, wobei aber innerhalb einer Schichtserie die Verhältnisse von marin (hoch) und nicht-marin (niedrig) erhalten bleiben. Noch bei alten praekambrischen Schichten liegen Verhältnisse vor, die sich mit den rezenten durchaus vergleichen lassen. Wir dürfen also wohl sagen, dass wir keine Anhaltspunkte besitzen für die Annahme, dass sich innerhalb der geologisch überblickbaren Zeit der Borgehalt oder der Salzgehalt des Meeres geändert hätte.

Goldschmidt und Peters (1932) haben schon einen Versuch gemacht, mit Hilfe des Borgehaltes die Fazies der Gesteine im Ruhrgebiet zu erforschen. Sie kamen zu dem Schluss, dass es nicht möglich sei, mit Hilfe des Borgehaltes die Fazies zu erschliessen. Bei den spektrographischen Bestimmungen von Goldschmidt und Peters wurden jedoch nur Unterschiede im Ausmass einer halben Grössenordnung erfasst, während Landergren sehr viel kleinere Unterschiede verwertet hat. Es erschien daher nicht ausgeschlossen, dass mit Hilfe mikrochemischer Methoden eventuell doch noch charakteristische Unterschiede zu finden wären. Dabei war es von vornherein nicht notwendig, dass diese Unterschiede an eine definierbare oder überhaupt an eine bestimmte Fazies geknüpft seien. Für praktische Zwecke war es lediglich notwendig, dass mit Hilfe des Borgehaltes bestimmte Horizonte deutlich von anderen Horizonten abgrenzbar seien, ähnlich wie ein Leitfossil einen stratigraphischen Wert haben kann, auch ohne dass man seine systematische oder bionomische Einordnung kennt.

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Die Untersuchung hat gezeigt, dass in den pelitischen Sedimenten derart abgrenzbare Horizonte vorkommen. Sie hat weiter gezeigt, dass die Borgehalte, in guter Übereinstimmung mit den Untersuchungen von Landergren, die Trennung mariner und limnischer Fazies gestatten. Auch die aus der Sowjet-Union gemeldete Anreicherung in manchen Ölschiefern konnte in bescheidenem Masse an einer fossilen Algengyttja, dem Kukkersit, bestätigt werden. Allerdings ist es für jeden Bereich nötig, die Methode an Proben bekannter Salinitätsfazies zu eichen; nicht der absolute Wert, sondern die Verhältnisse hoch: niedrig entscheiden.

Die gute Verwendbarkeit des Borgehaltes dürfte darauf zurückzuführen sein, dass die in Frage kommenden Borate unter den Verhältnissen der subaquatischen Bodenbildung (Halmyrolyse bzw. Thololyse), Diagenese und Verwitterung wenig löslich sind. Bei der Metamorphose, und zwar schon bei beginnender Metamorphose, kann dagegen eine Mobilisierung der Borate eintreten. Von den untersuchten devonischen Proben zeigt die eine Art, grau-grüne Schiefer mit marinen Fossilien, $B_2O_3$-Gehalte von 0,018 bzw. 0,020%; die andere Art, rote Schiefer mit Fischresten, Gehalte von 0,012 bzw. 0,013%. Multipliziert man diese Gehalte mit 2, so käme man zu normalen Gehalten für marines bzw. brackisches Wasser. Wenn also in dem Gebiet dieser bereits an Phyllite erinnernden Schiefer der Borgehalt vermindert erscheint, so ist doch das Verhältnis der Borgehalte immer noch so, wie es den Fossilien nach zu erwarten ist.

Es scheint also in der Bestimmung der Borgehalte eine Methode gegeben zu sein, die einerseits von Bedeutung ist für Korrelierung im Bergbau, andererseits aber auch geeignet ist, über die Salzgehaltsfazies des Ablagerungsraumes Aufschluss zu geben.

Eine qualitative Bestätigung fanden unsere Untersuchungen durch spektrographische Untersuchungen im Geologischen Institut der Universität Bonn (Brinkmann und Degens, 1956).

### 2. Ergebnis der Parallelisierung

Die Untersuchung zahlreicher karbonischer Schiefertone hat ergeben, dass zwischen den Borgehalten der Gesteine und der Salzgehaltsfazies ihrer Fauna ein direkter Zusammenhang besteht:

(1) Schiefertone mit marinen Fossilien 0,03–0,06% $B_2O_3$.
  (a) *Goniatites sphaericostriatus* BIS;
  (b) *Anthracoceras vanderbeckei* (SOW);
  *Pterinopecten papyraceus* SOW.;
  (c) *Lingula mytiloides* SOW.;
  (d) Foraminiferen (*Glomospira*, *Glomospirella*, *Ammodiscus*, *Hyperammina*).

(2) Schiefertone mit Süsswasser-Fossilien 0,005–0,015% $B_2O_3$.
  (a) Muscheln der Gattungen *Anthracosia* und *Naiadites*;
  (b) Ostracoden der *Carbonita*-Gruppe
  (c) *Planolites montanus* (R. Richter).

Abb. 1 zeigt die vertikale Verteilung der Borgehalte eines marinen Profiles in Abhängigkeit zur Fauna. In den unteren Lagen mit mariner Fauna (*Anthracoceras vanderbeckei*, *Pterinopecten papyraceus*, Conodonten, Foraminiferen) betragen die $B_2O_3$-Gehalte mehr als 0,03%. Im oberen Profilabschnitt sind die

$B_2O_3$-Gehalte durchschnittlich niedriger als 0,03%, mit Ausnahme der Lagen, die noch Foraminiferen führen. Noch 15 m über dem Flöz kommen Lagen mit wenigen Foraminiferen vor, die einen hohen Borgehalt haben (in Abb. 1 nicht eingezeichnet). Die Kurve der Borgehalte scheint somit ein deutliches Abbild der Fossilverteilung im Gestein zu sein.

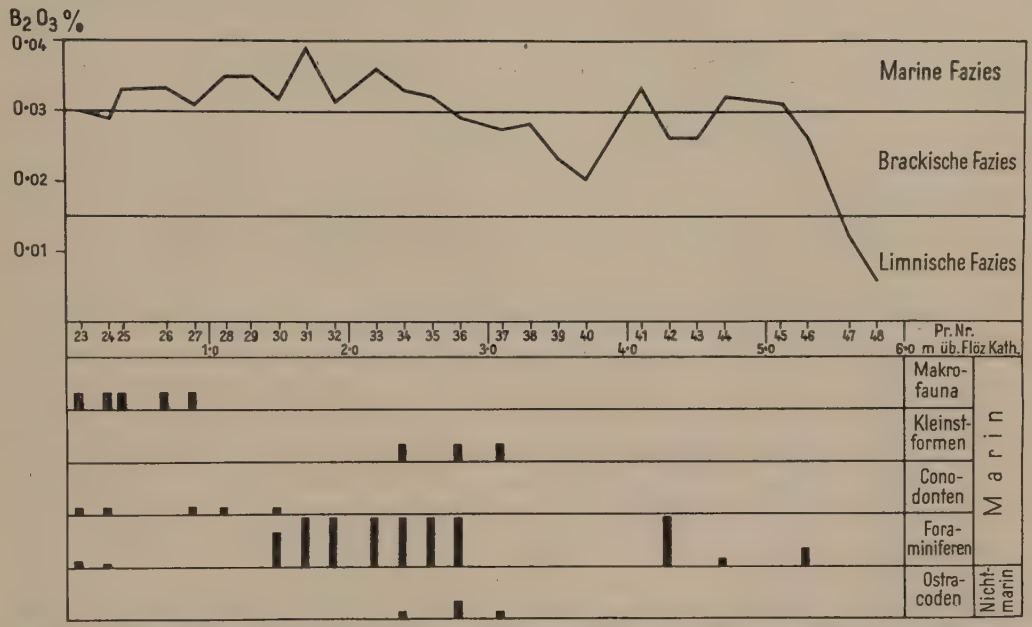


Abb. 1. Vertikale Verteilung der Borgehalte im marinen Katharina–Niveau (Westfal B, Essener Schichten). Zeche Victoria, H.–Querschlag nach Süden, 1. Sohle.

Für praktische Zwecke genügt das Ergebnis, dass marine Schiefertone höhere Borgehalte als nicht-marine Schiefertone haben. Ein Beispiel ist das marine Katharina-Niveau (Basis Westfal B), dessen hohe Borgehalte allein genügen würden, um eine Parallelisierung über grössere Entfernung durchzuführen. Die $B_2O_3$Gehalte dieses Niveaus betragen in den untersuchten Steinkohlengebieten von Westfalen, Aachen, Belgien und Nordfrankreich über 0,04% (Tabelle 1).

Ein weiteres Beispiel ist das marine Domina-(*Lingula*)-Niveau (Basis Horster Schichten), das mit Hilfe mariner Fauna bis zu einer Linie nachweisbar ist, die etwa quer durch das mittlere Ruhrgebiet verläuft. Östlich dieser Linie fehlen Anzeichen mariner Fauna. Dagegen ist in diesem Gebiet ein geringmächtiger Horizont mit wenigen Fischschuppen ausgebildet, der etwa eine gleiche stratigraphische Lage hat wie das Domina-(*Lingula*)-Niveau westlich der genannten Faziesgrenze. Die Borgehalte sind in diesem Horizont wesentlich höher als in benachbarten limnischen Horizonten. Sie nehmen ausserdem nach Westen zu, und erreichen unweit der Linie, wo die marine Fauna zu enden scheint, einen $B_2O_3$-Gehalt von 0,042% (Tab. 1). Der gleiche Borgehalt wurde für den marinen Abschnitt des Domina-(*Lingula*)-Niveaus im Grubenfeld der Zeche Westerholt festgestellt. Die beiden Horizonte scheinen miteinander identisch zu sein, der Ausfall mariner Fauna könnte mit den nach Osten abnehmenden Salzgehalten

(indiziert durch die in dieser Richtung abnehmenden Borgehalte) erklärt werden (Ernst, 1956). Bemerkenswert ist auch eine Aufspaltung des marin beeinflussten Fischschuppen-Horizontes (Tab. 1), die sich nach Westen in den Bereich des marinen Domina-(*Lingula*)-Niveaus fortzusetzen scheint.

In den Essener Schichten sind weitere marine Horizonte ausgebildet, die im Hangenden der Laura-Viktoria-Flözgruppe und über Flöz Zollverein 1 liegen. Beide Horizonte sind nur wenige Zentimeter mächtig und bestehen aus schwarzen, milden, fossilfreien Schiefertonen. Ihr Nachweis gelang bis vor kurzem nur mit Hilfe ihrer Borgehalte, neuerdings konnten aber Michelau und Tasch* den marinen Horizont über Flöz Zollverein 1 auch ausserhalb unseres Untersuchungsgebietes mit Hilfe von Foraminiferen auffinden. Eine nachträgliche Borbestimmung bestätigte den marinen Charakter der Schichten. Die Bildung dieser geringmächtigen marinen Horizonte scheint an kurzfristige Vorstösse von Meerwasser gebunden gewesen zu sein, wobei der Einschwemmung und Entfaltung mariner Fauna enge zeitliche Grenzen gesetzt waren.

Untersuchungen der Borgehalte von Proben aus anderen geologischen Formationen (Unterdevon, Unterkarbon, Tertiär) ergaben zwischen mariner und nichtmariner Fazies ähnliche charakteristiche Unterschiede wie bei karbonischen Schiefertonen (Tabelle 1).

Bei der Bor-Methode ergeben sich Fehlermöglichkeiten bei der Probenahme und bei der Aufbereitung der Proben. Es wurde erwähnt, dass marine Horizonte oft nur geringmächtig sind und keine deutlichen petrographische oder faunistische Unterschiedsmerkmale zu den umgebenden nicht-marinen Schiefertonen haben. Aus einer Einzelprobe kann hierbei nicht auf die Marinität oder Nicht-Marinität der Schichten geschlossen werden, vielmehr sind zur Abgrenzung der marinen Lagen Untersuchungen mehrerer Proben nötig. Einlagerungen in den Schiefertonen, wie Toneisensteine oder flächenhafter Pyritbelag auf Schichtflächen, sind bei der Aufbereitung der Proben möglichst vollständig zu entfernen, da sie Anlass zu Störungen bei der chemischen Analyse sein können. Bituminöse Schiefertone können gelegentlich höhere Borgehalte haben als dem ursprünglichen Salzgehalt im Ablagerungsgebiet entsprechen würde. Änderungen der Borgehalte durch borhaltige Minerale wie Turmalin, Datolit, Dumortierit oder Axinit sind bei karbonischen Schiefertonen unwahrscheinlich, da bisher nur Turmalin in sehr geringen Mengen in Karbonsandsteinen des Ruhrgebietes bekannt ist (Kneuper, 1957).

Die Borbestimmung versagt bei Sandsteinen und bei starksandigen Schiefertonen, da diese nur Spuren von Boraten enthalten. Bei Kalken, Dolomiten, Braun- und Steinkohlen sind Borbestimmungen mit Einschränkung möglich.

Die Untersuchung der Borgehalte erfolgte im Geochemischen Labor des Geologisch-Paläontologischen Institutes der Universität Frankfurt am Main (Bradacs) und im Chemischen Labor des Geologischen Landesamtes Nordrhein-Westfalen in Krefeld (Werner und Mitarbeiter). Zur Kontrolle wurden die Borgehalte gleicher Proben sowohl in Frankfurt als auch in Krefeld bestimmt, wobei die Frankfurter Werte meistens höher waren, und zwar im marinen Bereich

* *Über einen neuen schwachmarinen Horizont in den Essener Schichten des Ruhrgebietes.* (in Druck bei Glückauf, Essen).

Tabelle 1. $B_2O_3$-Gehalte der untersuchten Proben

Abkürzungen: Ausführung der Analysen: A = Geochemisches Labor des Geologisch-Paläontologischen Institutes der Universität Frankfurt am Main. B = Chemisches Labor des Geologischen Landesamtes Nordrhein-Westfalen. Scht. = Schieferton. Conod. = Conodonten. For. = Foraminiferen. Ostr. = Ostracoden. Z. = Zeche. Qu. = Querschlag. Abt. = Abteilung.

| Pr. Nr. | Geologische Formation Probenbeschreibung | Fundort | $B_2O_3$ (%) | |
|---|---|---|---|---|
| | | | A | B |
| | (1) Ordovizium | | | |
| A 55 | Kukkersit | Kohtla, Estland | 0,059 | |
| | (2) Devon, Gedinne | | | |
| A 61 | Grau-grüner Schiefer mit marinen Fossilien | Steinbr. Neue Mühle Lammersdorf. Hohes Venn | 0,020 | |
| A 62 | Roter Schiefer mit Fischresten | Osthang Jagen 105 Lendersdorf. Hohes Venn | 0,013 | |
| A 63 | Grau-grüner Schiefer mit marinen Fossilien | Eppenhain, Bl. Königstein, Taunus | 0,018 | |
| A 64 | Roter Schiefer mit Fischresten | Silverbach, 1 km NW von Eppenhain, Bl. Königstein. Taunus | 0,012 | |
| | (3) Karbon | | | |
| | 31. Marine Fazies | | | |
| | 311. Kulm III, *striatus*-Zone | | | |
| A 48 | Scht. m. *Goniatites sphaerico-striatus* BIS. | Innerste-Tal bei Clausthal. Harz | 0,056 | |
| | 312. Westfal B, Katharina-Niv. | | | |
| A 1 | Scht. mit *Lingula* sp. | Z. Werne, 5. westl. Abt. 730-m-Sohle | 0,040 | |
| A 2 | Scht. m. *Anthracoceras vanderbeckei* (SOW.) | Z. Victoria. H.-Qu. 1. Sohle | 0,035 | |
| A 24 | Scht. m. *Anthracoceras vanderbeckei* (SOW.) | Z. Fürst Hardenberg 8. Abt., Mittelort | 0,045 | |
| A 36 | Scht. m. *Anthracoceras vanderbeckei* (SOW.) | Z. A. v. Hansemann 4. östl. Abt., 1.Sohle | 0,040 | |
| A 56 | Scht. m. *Lingula* sp. | Z. Kaiserstuhl I 3. Abt.,6.Sohle | 0,040 | |
| A 57 | Scht. m. *Anthracoceras vanderbeckei* (SOW.) | Z. Constantin 4/5 3.Abt. | 0,050 | |
| A 38 | Scht. m. *Lingula* sp. | Z. Carl Alexander Baesweiler b.Aachen 2.östl.Qu.,2.Sohle | 0,043 | |
| A 31 | Scht. m. *Lingula mytiloides* SOW. | Gisement de la Campine, Charbonnage André Dumont | 0,047 | |
| A 32 | Scht. m. *Lingula mytiloides* SOW. | Bassin de Liège, Charbonnage de Marihaye | 0,044 | 0,035<br>0,034 |
| A 33 | Scht. m. *Lingula mytiloides* SOW. | District de Charleroi, Charbonnage du Poirier | 0,045 | 0,040 |

Tabelle 1 (*Fortsetzung*)

| Pr. Nr. | Geologische Formation Probenbeschreibung | Fundort | $B_2O_3$ (%) A | $B_2O_3$ (%) B |
|---|---|---|---|---|
| | (3) Karbon (*cont*). | | | |
| A 35 | Scht. | District du Couchant de Mons, Charbonnage de Bernissart | 0,048 | 0,036<br>0,034 |
| A 45 | Scht. m. *Lingula* sp. | Concession d'Anzin Groupe de Valenciennes | 0,050 | 0,035 |
| A 46 | Scht. m. *Lingula* sp. | Concession de Lens, Groupe de Lens/Lievin | 0,055 | |
| A 47 | Scht. m. *Lingula* sp. | Concession de Ligny, Groupe d'Auchel | 0,055 | 0,042 |
| | Katharina-Niveau<br>Vertikalprofil vom marinen zum limnischen Faziesbereich (Text-Abb. 1) | Z. Victoria, H.-Qu. 1. Sohle | | |
| B 23 | Scht. m. *Anthracoceras vanderbeckei* (SOW.), Conod., For., 1 nicht-marine Muschel | 0,1 m üb. Flöz Katharina | | 0,033<br>0,032 |
| B 24 | Scht. m. *Anthracoceras vanderbeckei* (SOW.), *Pterinopecten papyraceus* SOW., Conod., For. (*Glomospirella*) | 0,2 m üb. Flöz Katharina | | 0,029<br>0,029 |
| B 25 | Scht. m. *Anthracoceras vanderbeckei* (SOW.) | 0,4 m üb. Flöz Katharina | | 0,034<br>0,032 |
| B 26 | Scht. m. *Anthracoceras vanderbeckei* (SOW.) | 0,7 m üb. Flöz Katharina | | 0,034<br>0,033<br>0,031 |
| B 27 | Scht. m. *Anthracoceras vanderbeckei* (SOW.), Orthoceras?, Conod. | 0,9 m üb. Flöz Katharina | | 0,036<br>0,030<br>0,028 |
| B 28 | Scht. m. *Anthracoceras vanderbeckei* (SOW.), *Pterinopecten papyraceus* SOW., Conod. | 1,1 m üb. Floz Katharina | | 0,040<br>0,036<br>0,034 |
| B 29 | Scht. m. Conod. | 1,3 m üb. Floz Katharina | | 0,038<br>0,033 |
| B 30 | Scht. m. Conod., For. (*Ammodiscus, Glomospirella, Glomospira, Hyperammina*) | 1,5 m üb Flöz Katharina | | 0,033<br>0,030 |
| B 31 | Scht. m. *Lingula* sp., *Planolites* cf. *ophthalmoides* JESSEN, For. (überwiegend *Glomospirella*) | 1,7 m üb. Floz Katharina | | 0,041<br>0,041<br>0,037 |
| B 32 | Scht. m. For. (*Glomospirella*) | 1,9 m üb. Flöz Katharina | | 0,032<br>0,031 |
| B 33 | Scht. m. For. (*Glomospirella*) | 2,1 bis 2,2 m üb. Fl. Katharina | | 0,037<br>0,035 |
| B 34 | Scht. m. For. (*Glomospirella*), marine Kleinstformen, Ostr. (*Jonesina*-Gr., *Carbonita*-Gr.) | 2,4 m üb. Flöz Katharina | | 0,035<br>0,033<br>0,030 |

Tabelle 1 (*Fortsetzung*)

| Pr. Nr. | Geologische Formation Probenbeschreibung | Fundort | $B_2O_3$ (%) | |
|---|---|---|---|---|
| | | | A | B |
| B 35 | Scht. m. For. (*Ammodiscus, Glomospirella, Glomospira*) | 2,5 bis 2,6 m üb. Fl. Katharina. | | 0,033<br>0,033<br>0,031 |
| B 36 | Scht. m. *Planolites* cf. *ophthalmoides* JESSEN, For. (*Glomospirella*, marine Kleinstformen, Ostr. (*Jonesina*-Gr., *Carbonita*-Gr.) | 2,8 m üb. Flöz Katharina | | 0,032<br>0,027 |
| B 37 | Scht. m. marinen Kleinstformen, Ostr. (*Jonesina*-Gr., *Carbonita*-Gr.) | 3,0 bis 3,1 m üb. Fl. Katharina | | 0,029<br>0,026 |
| B 38 | Scht. | 3,3 m üb. Flöz Katharina | | 0,029<br>0,027 |
| B 39 | Scht. | 3,5 m üb. Flöz Katharina | | 0,025<br>0,024<br>0,020 |
| B 40 | Scht. | 3,7 m üb. Flöz Katharina | | 0,022<br>0,022<br>0,017 |
| B 41 | Scht. | 4,0 bis 4,1 m üb. Fl. Katharina | | 0,034<br>0,032 |
| B 42 | Scht. m. For. (*Glomospirella, Glomospira*) | 4.3 m üb. Flöz Katharina | | 0,027<br>0,024 |
| B 43 | Scht. | 4.5 m üb. Flöz Katharina | | 0,028<br>0,026<br>0,025<br>0,024 |
| B 44 | Scht. m. For. (*Ammodiscus, Glomospirella*) | 4,7 m üb. Flöz Katharina | | 0,034<br>0,031<br>0,030 |
| B 45 | Scht. | 5,1 m üb. Flöz Katharina | | 0,033<br>0,029 |
| B 46 | Scht. m. For. | 5,3 m üb. Flöz Katharina | | 0,028<br>0,027<br>0,026<br>0,025 |
| B 47 | Scht. | 5,6 m üb. Flöz Katharina | | 0,012<br>0,011 |
| B 48 | Scht. | 5,8 m üb. Flöz Katharina | | 0,007<br>0,006<br>0,005 |
| | 313. Westfal B, Niveau 17 K (Laura-Viktoria-Flözgr.) Vertikalprofil vom marinen zum limnischen Faziesbereich | | | |
| A 21 | Scht., 0 bis 0,01 m üb. Flöz | Z. Fürst Hardenberg 8. Abt., Mittelort | 0,028 | 0,036 |
| A 22 | Scht., 0,01 bis 0,02 m üb Flöz | Z. Fürst Hardenberg 8. Abt., Mittelort | 0,020 | |

Tabelle 1 (*Fortsetzung*)

| Pr. Nr. | Geologische Formation Probenbeschreibung | Fundort | $B_2O_3$ (%) | |
|---|---|---|---|---|
| | | | A | B |
| A 23 | Scht. m. nicht-mar. Muscheln 0,02 bis 0,05 m üb. Flöz | Z. Fürst Hardenberg 8. Abt., Mittelort | 0,014 | |
| A 60 | Scht. 0 bis 0,02 m üb. Flöz | Z. Minister Stein 4. Abt., 4. Sohle | 0,031 | |
| | 314. Westfal B, Zollverein 1 -Niveau Vertikalprofil vom marinen zum limnischen Faziesbereich | | | |
| A 58 | Scht., 0 bis 0,03 m üb. Flöz | Z. Minister Stein Östl. Muldenstrecke 4. Sohle | 0,035 | |
| A 59 | Scht., 0,03 bis 0,06 m üb. Flöz | Z. Minister Stein Östl. Muldenstrecke 4. Sohle | 0,016 | |
| | 315. Westfal B, Domina-(*Lingula*)-Niveau Unterer Horizont (I) | | | |
| A 14 | Scht. m. wenigen Fischschuppen | Z. Werne, 5. westl. Abt. 730-m-Sohle | 0,022 | |
| A 15 | Scht. m. wenigen Fischschuppen | Z. Teutoburgia, H.-Abt. Ort 2, Flözstrecke E nach Westen, Hgd. 22 K | 0,030 | 0,030 |
| A 39 | Scht. | Z. Recklinghausen II Qu. 2 Ost nach Norden 4. Sohle, Hgd. Fl. 69 K | 0,042 | 0,030 |
| | A 27 bis A 29 Vertikalprofil | | | |
| A 27 | Scht. m. *Lingula* sp. | Z. Westerholt 0 bis 0,15 m üb. Fl. L | 0,042 | |
| A 28 | Scht. m. *Lingula* sp. | Z. Westerholt 0,5 bis 0,55 m üb. Fl. L Z. Westerholt | 0,030 | |
| A 29 | Scht. | Z. Westerholt 1,0 bis 1,1 in üb. Fl.L | 0,029 | 0,032 |
| | Oberer Horizont (II) | | | |
| A 16 | Scht. | Z. Teutoburgia, H.-Abt. 1. Sohle, Hgd. Flöz E | 0,027 | |
| | A 40 bis A 41 Vertikalprofil vom marinen zum limnischen Faziesbereich | | | |
| A 40 | Scht. | Z. Recklinghausen II Qu. 2 Ost nach Norden 4. Sohle, Hgd. Flöz 40 K 0 bis 0,10 m | 0,029 | |

Tabelle 1 (*Fortsetzung*)

| Pr. Nr. | Geologische Formation Probenbeschreibung | Fundort | $B_2O_3$ (%) | |
|---|---|---|---|---|
| | | | A | B |
| A 41 | Scht. | Z. Recklinghausen II Qu. 2 Ost nach Norden 4. Sohle, Hdg. Flöz 40 K 0,20 bis 0,25 m | 0,021 | |
| | 316. Westfal A, Hauptflöz | | | |
| A 51 | Dolomit, marin | Zeche Hubertus | 0,016 | |
| | 32. Brackische Fazies | | | |
| A 17 | Scht. m. nicht-marinen Muscheln | Z. Teutoburgia, H.-Abt. 1. Sohle, zwischen Flöz G und Flöz H | 0,016 | |
| A 25 | Scht. m. Ostr. (*Jonesina*-Gruppe) | Z. Fürst Hardenberg 8. Abt., Mittelort, Lgd. Flöz 25 K | 0,018 | |
| A 52 | Scht. m. *Anthraconauta minima* (HIND) | Steinbruch an der Verbandsstrasse Essen-Heisingen Hgd. Flöz Luise | 0,018 | |
| | 33. Limnische Fazies | | | |
| A 4 | Scht. m. *Naiadites* cf. *subtruncatus* | Z. Victoria, H. Qu., 1. Sohle, Laura-Viktoria-Flöze | 0,015 | |
| A 5 | Scht. m. nicht-marinen Muscheln | Z. Victoria, H. Qu., 1. Sohle, Hgd. Flöz 15K | 0,008 | |
| A 6 | Scht. m. nicht-marinen Muscheln | Z. Victoria, H. Qu., 1. Sohle, ± 30 m über Flöz Katharina | 0,008 | |
| A 7 | Scht. m. Ostr. (*Carbonita*-Gruppe) | Z. Werne, 5. westl. Abt. 730-m-Sohle Hgd. Flöz 22 | 0,009 | |
| A 8 | Bituminöser Scht. m. Fischresten | Z. Werne, 4. westl. Abt. Ort. 2, Hgd. Fl. Zollv. 7 | 0,015 | |
| A 9 | Scht. m. Ostr. | Z. Werne, 5. westl. Abt. 730-m-Sohle, Hgd. Fl. W | 0,009 | |
| A 10 | Bituminöser Scht. m. Fischresten | Z. Werne, 5. westl. Abt. 730-m-Sohle Hgd. Flöz Zollverein 7 | 0,009 | |
| A 11 | Scht. m. nicht-marinen Muscheln | Z. Victoria, H. Qu. 1. Sohle, Hgd. Flöz 28 K | 0,010 | |
| A 12 | Scht. m. nicht-marinen Muscheln | Z. Victoria, H. Qu. 1. Sohle, Hgd. Flöz 15 K | 0,008 | |
| A 13 | Scht. m. nicht-marinen Muscheln | Z. Victoria, H. Qu. 1. Sohle Hgd. Flöz Zollverein 1 | 0,007 | — |

Tabelle 1 (*Fortsetzung*)

| Pr. Nr. | Geologische Formation Probenbeschreibung | Fundort | $B_2O_3$ (%) A | $B_2O_3$ (%) B |
|---|---|---|---|---|
| A 18 | Bituminöser Scht. | Z. Teutoburgia, H. Abt. Ort 2, Hgd. Fl. Zollv. 8 | 0,011 | |
| A 19 | Bituminöser Scht. m. Fischresten | Z. Werne, 5. westl. Abt. 730-m-Sohle Hgd. Flöz Zollverein 1 | 0,012 | |
| A 20 | Bituminöser Scht. m. Fischresten | Z. Victoria, H. Qu. 1. Sohle Hgd. Flöz Zollverein 7 | 0,012 | |
| A 26 | Scht. | Z. Fürst Hardenberg 8. Abt., Mittelort Laura-Viktoria-Flöze | 0,011 | |
| A 30 | Scht. m. nicht-marinen Muscheln u. *Planolites montanus* R. RICHTER | Z. Victoria, H. Qu. 1. Sohle Hgd. Flöz Zollverein 1 | 0,009 | |
| A 42 | Scht. m. nicht-marinen Muscheln | Z. Recklinghausen II Qu. 2 Ost nach Norden 4. Sohle, Hgd. Flöz K. | 0,011 | |
| A 50 | Süsswasser-Dolomit (Untere Horster Schichten) | Z. Franz Haniel | 0,009 | |
| A 54 | Scht. m. Ostr. (*Carbonita*-Gruppe) (4) Tertiär | Saarländisches Steinkohlengebiet | 0,010 | |
| A 65 | Braunkohle, marin beeinflusst | Z. Frimmersdorf Süd Flöz Morken II | 0,019 | |
| A 66 | Braunkohle, marin beeinflusst | Z. Frimmersdorf Süd Flöz Morken I | 0,018 | |
| A 67 | Braunkohle, terrestrisch (A 65 u. A 66 nach Ca/Mg-Verhältnis marin) | Z. Frimmersdorf Süd Flöz Frimmersdorf Oberkante | 0,011 0,008 | |

bis zu 0,015%; der Gang zwischen limnischen und marinen Schichten war jedoch derselbe. Dieser Unterschied in den Analysen dürfte im Wesentlichen auf der unterschiedlichen Methodik beruhen.

### 3. Chemische Methode

Zur Bestimmung kleiner Borsäuregehalte stehen zahlreiche kolorimetrische Methoden zur Verfügung, wie die Durchsicht des Schrifttums der letzten Jahre zeigt. Vorgeschlagen wird die Anwendung von Carmin, Curcumin, Chinalizarin, Chromotrop 2B, Anthrimid u.a. Da das Anthrimid von vielen Autoren als das empfindlichste Reagenz bezeichnet wird, entschlossen wir uns für Anwendung des letzteren. Eine direkte Bestimmung der Borsäure im Sodaaufschluss des Gesteins ist nicht durchführbar, da die grosse Alkalimenge die Anthrimidreaktion stört. Aus

demselben Grunde ist die Auswahl der Destillationsmethode wichtig, denn bei der oft vorgeschlagenen Erhitzung bis zum Rauchen der Schwefelsäure sind zur Neutralisierung der mit übergehenden Säure vor dem Eindampfen grössere Alkalimengen erforderlich.

Die von Roth und Beck (1954) angegebene Destillation im Methanoldampfstrom ist nach unseren Erfahrungen die sicherste Methode. Der Borsäuremethylester geht quantitativ über und beim Eindampfen des Destillates braucht kein Alkali zugesetzt zu werden (es werden lediglich 10 ml 0,1 N $Ca(OH)_2$-Lösung vorgelegt). Zur Entwicklung der Bor-Anthrimid-Färbung erhitzen wir im

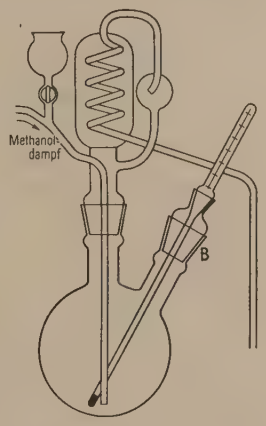


Abb. 2. Fur Serienuntersuchungen modifizierter Destillationsapparat.

Thermostaten 5 Stunden auf 70° C, wie von Baron (1954) angegeben. Auf diese Weise, und durch einen Zusatz von Hydrazinsulfat, wird die sonst gelegentlich auftretende Braunfärbung des Anthrimids sicher verhindert. Um eine Überhitzung im Destillationskolben zu vermeiden, erwies es sich als praktisch, Schwefelsäure und Methanol vor dem Zugeben zu mischen und zu kühlen. Nur die Schwefelsäure, die zum Lösen des Sodaaufschlusses erforderlich ist (etwa 5 ml), wird vorher eingefüllt. Zur Aufstellung der Eichkurve werden vorgegebene Borsäuremengen destilliert. Dadurch überzeugt man sich vom quantitativen Übergehen des Borsäuremethylesters sowie vom einwandfreien Arbeiten der Apparatur. Als Einwaage wählt man zweckmässigerweise 350 mg; der Bereich von 0,005 bis 0,05% $B_2O_3$ entspricht dann etwa zur Anfärbung gelangenden Mengen von 0,5–5$\gamma$ Bor.

Die Apparatur wurde in Hinblick auf Serienuntersuchungen etwas abgeändert (Abb. 2). Der Kühler braucht nicht abgenommen zu werden. Durch den Schliff B, der auch zum Einbringen des Aufschlusses dient, wird nach Beendigung der Destillation mit Hilfe einer Wasserstrahlpumpe der Kolbeninhalt abgesaugt. Darauf wird mit Methanol ausgespült (Spritzflasche), wieder abgesaugt, und Reste des Methanols durch gelindes Erwärmen vertrieben. Auf den Zwischenkühler kann verzichtet werden, da beim Lösen des Schmelzkuchens im Destillierkolben mit Schwefelsäure unter leichtem Erhitzen keine Borverluste auftreten (Baron, 1954). Da die restliche Schwefelsäure mit dem Methanol vorher gemischt und abgekühlt wird, tritt vor der Destillation keine Erhitzung und damit kein Verlust von Borsäuremethylester auf. Die zur kolorimetrischen Bestimmung erforderlichen

10 ml des Destillates werden in Quarzkolben mit Schliffstopfen eingedampft, der Rückstand mit genau 5 ml Schwefelsäure gelöst und anschliessend mit genau 5 ml Anthrimidreagenz versetzt. Die Kolben werden mit aufgesetztem Schliffstopfen in den Thermostaten gestellt. Da das Auseinandernehmen der Apparatur beim Reinigen sowie das Umfüllen der zu kolorimetrierenden Lösung in Messkolben entfällt, werden Verunreinigungsmöglichkeiten sowie Zeitbedarf der Analysen erheblich verringert.

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# Radioactive waters from sediments

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**Abstract**—Determinations of radioactivity by measuring the radon content in a number of Yugoslav mineral waters have shown that their radioactivity depends on the geologic age of the sediments through which they are flowing. Those waters which issue from Carboniferous or Cretaceous strata show a distinctly higher radioactivity due to a higher content of uranium in those sediments.

Part of the content in radioactive substances of the waters is deposited in sinters that sometimes accumulate around the springs. In those deposits uranium is, as a rule, not in radioactive equilibrium with its daughter elements. Particularly in cases of calcareous sinters and ochres there are generally more ionium and radium present than would correspond to the radioactive equilibrium. Only deposits from waters containing hydrogen sulphide contain mainly uranium. Water that passes through such sinters shows a greater radioactivity than the original water. The highest factor of enrichment (7.27) was found in the thermal water of Višegrad.

A certain relationship between the radioactivity of a mineral water and the age of the sediments it is flowing through has been pointed out in a previous publication (Miholić, 1952). It was then stated that waters issuing from sediments belonging to the Carboniferous and Cretaceous show, on the average, a higher radioactivity than those which flow from sediments belonging to other geologic systems. This phenomenon would point to a greater amount of uranium contained in Carboniferous and Cretaceous sediments, particularly in bituminous schists and limestones. A number of investigations made since the publication of the paper seems to support this view.

The Illinois black shale in which Ostrom, Hopkins, White and McVicker (1955) found up to 170 p.p.m. of uranium is of Carboniferous age. Tourtelot (1956) described a hard black shale of Upper Cretaceous age, rich in organic matter, full of scales and bones of fish and with finely disseminated pyrite, which when unaltered contained in places as much as 100 p.p.m. uranium, while in those places where the upper part of the shale has been altered by pre-Oligocene weathering, the lower parts of it contain up to 1000 p.p.m. equivalent uranium and 300 p.p.m. uranium. The disequilibrium between equivalent uranium and the uranium content of the shales is believed to have been caused by a relatively recent leaching of uranium from the present out-crops by acid waters derived from the weathering of the pyrite, and a residual concentration of radium salts seems to have taken place. In the Black Hills, Butte County, South Dakota, the Fall River sandstone of Lower Cretaceous age contains according to Vickers (1957) 1000–2000 p.p.m. of uranium in places. The uranium was probably deposited originally from ground water that moved down-dip and gradually changed from an oxidizing solution near the surface to a mildly reducing solution at depth. In the widespread Upper Cretaceous algal limestone in Wyoming, Love (1953) found up to 1500 p.p.m. uranium. Even the carnotite deposits of the Colorado plateau, where the uranium is found today in Jurassic and Triassic strata, seem to have derived from overlying marine sediments of Cretaceous age which in many places

have been later eroded away. This would be confirmed by the results of the investigations by Stieff (1953) who determined the age of the uranium as Upper Cretaceous. In the Colorado front range Goldstein (1957) described an occurrence of uranium ore near Morrison, Jefferson County, Colorado in the Dakota formation consisting of sandstone and shale which belongs to the Lower Cretaceous and in which all the presently known uranium in the region has been found. In the upper part of the Dakota formation near a fault the uranium content averages in places 0·25 per cent. The uranium ore occupies only the footwall side of the fault which would suggest down-dip percolating groundwater carrying some uranium in solution.

In recent years a great many new determinations of the radioactivity in mineral waters have been made in different parts of Yugoslavia which in the main corroborate the previous findings, as can be seen from Table 1 which gives the age of the sediments from which the different waters issue as well the amount of radioactivity found.

In Bosnia a number of mineral waters issue from serpentine and in Macedonia several from Pre-Cambrian ortho-gneisses. Although these waters do not flow from sediments they are included in the table for comparison to show that waters from igneous rocks, as a rule, do not always show a higher radioactivity. This applies particularly to the ortho-gneisses of Mt. Kožuf in Macedonia which contain 4 p.p.m. of uranium and still show only a weak radioactivity.

From the data in the table the average radioactivity of the investigated mineral waters was calculated and found to be: Carboniferous 4·994 n c/l., Triassic 0·590 n c/l., Jurassic 0·651 n c/l., Cretaceous 17·78 n c/l., Eocene 0·4459 n c/l., Oligocene 0·2316 n c/l. and Miocene 0·028 n c/l. There are two distinct maxima for the Carboniferous and the Cretaceous. This relationship even proved a certain help while prospecting for uranium.

In the course of those investigations another phenomenon was observed: waters which flow through their own sediments often get considerably enriched in their radioactivity, a fact that has been noticed already by Genser (1933). This increase can be explained by the enrichment of the sediments in radioactive elements (uranium, ionium, radium) deposited from the water itself.

While in its accumulations in schists belonging to the Carboniferous and the Cretaceous uranium is usually in equilibrium with the products of its radioactive decay, as has been shown by Breger (1955) for some Cretaceous sediments, this is rarely the case with recent deposits from mineral waters. Particularly in cases of calcareous sinters and ochres there is generally more ionium and radium present than would correspond to the radioactive equilibrium. Only deposits from waters containing hydrogen sulphide contain mainly uranium (often partly in organic binding).

One of the first to study the accumulation of radioactive substances in ochres deposited from springs was Heinrich (1921) who also pointed out the compound nature of the radioactivity shown by the ochres. Genser (1933) found in the ochre deposited from a radioactive source in Oberschlemma in Germany greater quantities of radium (0·0283 p.p.m.) than would correspond to a radioactive equilibrium with the uranium present (4·9 per cent U). He ascribes it to secondary

enrichment. As the water is acid and contains sulphates, it leaches some uranium from the deposit, while practically all radium is precipitated. Schwille (1957), using a scintillometer, found a considerably increased radioactivity in the ochre deposited by the mineral waters in Bad Neuenahr and Bad Kreuznach.

The accumulation of radioactive elements in the mineral mud has also been noticed by Szabó (1957a), who investigated mineral waters in Rumania and found in Băile Herculane some springs considerably more radioactive (up to 21·46 n c/l.) than others (averaging 0·5 n c/l.) due to enrichment of the radioactive elements in the mud which contains $12{\cdot}4 \times 10^{-6}$ p.p.m. of radium. Szabó (1957b) also found in the calcareous sinters of the acidulated springs in Borsec $0{\cdot}90–6{\cdot}60 \times 10^{-6}$ p.p.m. of radium and in the ochre deposits at the same springs $3{\cdot}10 \times 10^{-6}$ p.p.m. of radium. Szabó and Soo (1957) investigated the mineral springs of Sîngeorz-băi, where the sources issuing on the plateau formed by the calcareous sinter show a low radioactivity of 0·23–0·43 n c/l., while the two springs issuing at the foot of the sinter deposit, which contains $12{\cdot}9–15{\cdot}3 \times 10^{-6}$ p.p.m. of radium, gave 24·47 and 29·97 n c/l. Szabó (1957c) considers that the radium concentrations in the Rumanian mineral waters have biological and not chemical causes.

Schlundt (1935) determined radiometrically the radioactivity of the calcareous sinters from Hot Springs, Arkansas and found $1392–3751 \times 10^{-6}$ p.p.m. of radium. In the United States the procedure now commonly employed for the determination of uranium in deposits from mineral waters is to determine the radioactivity of a sample radiometrically and express it as equivalent uranium (eU) and then to determine uranium fluorometrically (U). The difference between eU and U is assumed to be due to radium in excess to the radioactive equilibrium. Thus it was found that the calcareous sinter on the Allen property, Kern County, California contains 0·75 per cent eU and 0·008 per cent U (Walker, Lovering and Stephens, 1956), while the calcareous sinter at the Jemez Springs, Sandoval County, New Mexico contains 0·006 per cent eU and 0·002 per cent U (Lovering, 1956).

In recent sinters of the Tamagawa Hot Spring, Japan, Minami, Saito and Ishimori (1952) found that the decomposition products of radon are not in equilibrium with radium, whereas in old sinters the equilibrium is almost reached.

The deposition of precipitates from mineral waters is governed principally by two factors: the hydrogen ion concentration expressed as pH and the redox potential Eh. Three cases have been studied: (1) Deposits formed under oxidizing conditions from slightly alkaline solutions (calcareous sinters), (2) Deposits formed under oxidizing conditions from slightly acid solutions (ochres), and (3) Deposits formed under reducing conditions in presence of hydrogen sulphide and/or organic matter.

1. *Deposits formed under oxidizing conditions* (Eh = +0·05 *to* 0 V) *from slightly alkaline solutions* (pH = 7·5–9)

Under those conditions the uranium ion is, as a rule, present in the water as the uranyl ion ($UO_2^{++}$), which is soluble in waters containing the carbonate ion. This is almost always the case. Part of the uranium ion gets, however, adsorbed on ferric hydroxide often precipitated together with calcium carbonate in calcareous

sinters. On the other side radium is precipitated completely together with barium sulphate. The mechanism of this coprecipitation has been studied by Doerner and Hoskins (1925) who found that in the presence of a large excess of barium over radium—a condition fulfilled in most mineral waters—sulphate ions will precipitate radium even though the solubility product of radium sulphate is not exceeded. This was further investigated by Marques (1934) and recently by Gordon and Rowley (1957) who showed that the logarithmic distribution coefficient $\lambda$ for Ba/Ra in precipitates is greater at 20°C ($\lambda = 1{\cdot}69$) than at 90°C ($\lambda = 1{\cdot}21$). Thus the precipitation of radium will be more complete in deposits formed from cold mineral waters. As the amount of unadsorbed uranium on ferric hydroxide ($1–2 \times 10^{-8}$) (Rodden and Warf, 1950) exceeds the solubility product of barium sulphate ($1{\cdot}2 \times 10^{-10}$) it follows that sinters deposited from waters containing uranium and radium in radioactive equilibrium will in most cases contain more radium than corresponds to this equilibrium. Holland and Kulp (1954) studied the adsorption of radioactive elements on sediments from sea water and found that the fraction of radioactivity remaining after the separation of the sediment from water was independent of the total amount of radioactive elements and was thus in agreement with the law of mass action. They also found that ionium was selectively adsorbed on sediments, leaving the uranium behind. Radium was not adsorbed sufficiently to be in equilibrium with the ionium but was more strongly adsorbed.

The thermal water of Fojnica in Bosnia (Table 1, nos. 49–53) (Miholic, 1956) issues from a secondary fault in the dark Carboniferous schists 40 m above the valley floor on the west boundary of an extensive (about 50 acres) terrace of porous calcareous sinter which it has deposited and which is widely used as a building material. The sinter lies in places almost 30 m thick. From the fault the thermal water flows through the sinter in a south-easterly direction. This was established by chlorination of the thermal water issuing from the fault. On the terrace there are several springs among them: the spring in the Cave, the spring in the village of Banja, and finally the spring at the SE end of the terrace in the gorge. The radioactivity of the water increases with the distance from the fault from 3·604 n c/l. to 17·82 n c/l., due to secondary enrichment, while there is a decrease of calcium from 68·0 to 62·0 p.p.m. and of magnesium from 16 to 13 p.p.m., which have been partly deposited in the sinter. There is also a decrease in temperature from 29·3°C to 21·0°C.

The spa of Višegrad in Bosnia (Table 1, nos. 85 and 86) (Miholić, 1957) lies in the gorge of the brook Banja 4·5 km NNE from the town of Višegrad. The water issues from serpentine, but as calcium predominates in it and has formed an extensive calcareous sinter terrace, the material of which has yielded an excellent building stone, it is more probable that it flows from Upper Cretaceous limestone which covers great areas in the vicinity of the spa. There are two springs: first Sokolović' Bath, issuing from a fault on the slope about 10 m above the bottom of the valley, and second the Caid's Bath on the left bank of the brook to which the water flows through the calcareous sinter. By flowing through the sinter the water has increased its radioactivity from 2·530 to 18·38 n c/l., giving an enrichment factor of 7·27, the highest observed so far. At the same time the

water lost some calcium (from 71·1 to 55·6 p.p.m.) and iron (from 5·6 to 0·6 p.p.m.) while the temperature decreased from 34·2°C to 33·7°C.

In Lešće in Croatia (Table 1, nos. 35–37) a thermal spring (34·2°C) issues directly from a NW–SE fault in Upper Cretaceous limestone with a radioactivity of 3·277 n c/l. Farther to the north-west there are two other springs flowing from the calcareous sinter the water has deposited with temperatures of 29·6°C and 30·2°C and radioactivities of 3·850 n c/l. and 3·851 n c/l. respectively.

2. *Deposits formed under oxidizing conditions* (Eh = +0·58 *to* +0·22 V) *from slightly acid solutions* (pH = 4·0–6·0) (*ochre deposits*)

In slightly acid (pH > 3) solutions in an oxidizing environment the hexavalent uranyl-ion $UO_2^{2+}$ is adsorbed on colloidal ferric hydroxide which forms at pH = 3. The experiments made by Barton (1956) have shown that the uranium is in fact adsorbed and not precipitated. The obtained curve agreed well with that predicted by the Freundlich equation. Upon crystallization of the adsorbent, the uranium forms discrete uranium minerals within the former adsorbent. This has been shown by Lovering (1955) who observed that limonite which contains 0·05 per cent of uranium or more generally exhibits in thin sections distinct uranium minerals. He attributes this to the expulsion of adsorbed uranium during the crystallization of the iron oxide. On further ageing goethite yields uraniferous magnetite and hematite like the deposits at the Prince Mine, Lincoln County, New Mexico described by Walker and Osterwald (1956). Samples of the magnetite–hematite ore gave, respectively 0·023, 0·016, 0·044 per cent equivalent uranium and 0·015, 0·012, 0·031 per cent uranium.

In Srebrenica in Bosnia (Table 1, nos. 80–84) the spring "Eye Water" issues from an old mine in the gorge on the left bank of the brook Crvena Rijeka (Red River) from dark Carboniferous schists with a pH = 3, an iron content of 1369 p.p.m. and a radioactivity of 2·104 n c/l. Because of its strong acidity the water does not deposit any iron, but nearby there are considerable deposits of ochre estimated at about 20,000 tons. From this deposit a spring issues (Veliki Guber) with a pH = 5, where the iron content has fallen to 123·2 p.p.m., but the radioactivity increased to 7·02 n c/l. Farther down in the valley there is another spring (Mali Guber) from a smaller deposit of ochre. The water shows a pH = 4, contains 408·8 p.p.m. of iron and has a radioactivity of 3·578 n c/l.

3. *Deposits formed under reducing conditions* (Eh = −0·18 *to* −0·22 V) *in presence of hydrogen sulphide and/or organic matter in neutral or slightly alkaline* (pH = 7–9) *solution* (Krumbein and Garrels, 1952)

A mechanism of precipitation of uranium in a reducing medium has been suggested by Goldschmidt and studied in detail by McKelvey, Everhart and Garrels (1955) who showed that uranium may be transported in solution as $U^{6+}$ and precipitated as $UO_2$ by a reduction reaction. Reducing factors are: hydrogen sulphide, sulphur dioxide and organic matter. The redox potential for $U^{4+}$ is so low (Eh = +0·05 V at pH = 7) that only carbonaceous matter or hydrogen sulphide could reduce uranyl solutions at temperatures below 100°C (Gruner, 1956).

Table 1*

| Sample no. | Location | Stratigraphic age of source rock | Temperature (°C) | Radioactivity (Mache units) | Radioactivity (n c/l.) |
|---|---|---|---|---|---|
| | *Slovenia:* | | | | |
| 1 | Dobrna | Triassic | 35·4 | 1·658 | 0·604 |
| 2 | Rogaška Slatina | Miocene | 9·3 | 0.076 | 0·028 |
| 3 | Medijske Toplice | Triassic | 23·6 | 1·09 | 0·397 |
| 4 | Rimske Toplice | Carboniferous | 35·7 | 10·17 | 3·701 |
| 5 | Laško | Triassic | 35·3 | 1·384 | 0·5037 |
| 6 | Celje | Andesite | 9·2 | 4·99 | 1·82 |
| | Čatež | Carboniferous | | | |
| 7 | Main Source | | 51·4 | 10·72 | 3·901 |
| 8 | Well No. 3 | | 57·0 | 9·809 | 3·570 |
| 9 | Well No. 1 | | 57·9 | 10·26 | 3·735 |
| | *Croatia:* | | | | |
| 10 | Varaždinske Toplice | Triassic | 56·1 | 1·743 | 0·6343 |
| 11 | Harina Zlaka | Carboniferous | 33·5 | 11·24 | 4·09 |
| 12 | Kamena Gorica | Triassic | 22·7 | 1·357 | 0·4941 |
| | Tuheljske Toplice | Triassic | | | |
| 13 | Cliff Spring | | 32·4 | 1·234 | 0·448 |
| 14 | Swamp Spring | | 31·0 | 1·227 | 0·448 |
| | Krapinske Toplice | Triassic | | | |
| 15 | Jacob's Bath | | 39·1 | 0·563 | 0·205 |
| 16 | Popular Bath | | 41·4 | 0·696 | 0·253 |
| 17 | Šemnica | Triassic | 31·0 | 3·792 | 1·097 |
| 18 | Sutinske Toplice | Triassic | 35·9 | 1·296 | 0·472 |
| | Stubičke Toplice | Cretaceous | | | |
| 19 | Main Spring | | 53·4 | 3·16 | 1·15 |
| 20 | Maximilianeum | | 36·7 | 3·64 | 1·32 |
| 21 | Spring at the weir | | 30·7 | 19·99 | 7·27 |
| 22 | Podsused | Triassic | 17·2 | 1·19 | 0·432 |
| 23 | Čučerje | Cretaceous | 15·4 | 6·513 | 2·371 |
| 24 | Zelina | Cretaceous | 24·2 | 8·420 | 3·065 |
| 25 | St. Helena | Carboniferous | 26·0 | 1·967 | 0·716 |
| 26 | Toplica near St. Jana | Triassic | 24·7 | 3·549 | 1·292 |
| | Daruvar | Triassic | | | |
| 27 | Anthony's Bath | | 45·9 | 0·7891 | 0·2872 |
| 28 | Spring of the Central Mud-Bath | | 43·2 | 0·9059 | 0·3297 |
| 29 | John's Bath | | 44·7 | 0·6509 | 0·2369 |
| 30 | Spring of the Popular Mud-Bath | | 37·0 | 4·806 | 1·750 |
| 31 | Maria's Bath | | 42·0 | 2·187 | 0·7960 |
| 32 | Cold Spring | | 35·5 | 5·081 | 1·850 |
| 33 | Spring on the road | | 45·8 | 2·427 | 0·8830 |

* In cases where the radioactivity of a spring has been determined several times, only the last value is given.

Table 1 (*continued*)

| Sample no. | Location | Stratigraphic age of source rock | Temperature (°C) | Radioactivity | |
|---|---|---|---|---|---|
| | | | | (Mache units) | (n c/l.) |
| | *Croatia: (contd.)* | | | | |
| 34 | Velika | Triassic | 28·0 | 0·699 | 0·254 |
| | Lešće | Cretaceous | | | |
| 35 | Bath | | 34·2 | 9·002 | 3·277 |
| 36 | Swimming Pool | | 29·6 | 10·58 | 3·851 |
| 37 | Spring at the Old Mill | | 30·2 | 10·58 | 3·850 |
| | Istarske Toplice | Cretaceous | | | |
| 38 | Spring in the Bath | | 31·6 | 137·5 | 50·05 |
| 39 | Spring in the Cave | | 21·4 | 134·8 | 49·07 |
| 40 | Spring on the Meadow | | 15·3 | 600·2 | 218·5 |
| 41 | Vretenica on the Island of Krk | Cretaceous | 12·2 | 1·450 | 0·530 |
| 42 | Kruševo near Obrovac | Eocene | 20·5 | 0·965 | 0·351 |
| 43 | Split | Eocene | 21·3 | 1·45 | 0·530 |
| 44 | Vela Luka on the Island of Korčula (Kalac) | Cretaceous | 18·5 | 2·025 | 0·7371 |
| 45 | Mokošica | Cretaceous | 16·4 | 6·58 | 2·40 |
| | *Bosnia:* | | | | |
| 46 | Ilidža | Triassic | 55·3 | 0·6249 | 0·2269 |
| 47 | Blažuj | Triassic | 16·5 | 1·672 | 0·6085 |
| 48 | Kiseljak | Triassic | 12·2 | 0·278 | 0·101 |
| | Fojnica | Carboniferous | | | |
| 49 | Spring of the Old Bath | | 29·3 | 9·900 | 3·604 |
| 50 | Spring in the Cave | | 29·6 | 16·79 | 6·11 |
| 51 | Spring in the village | | 28·9 | 28·88 | 10·69 |
| 52 | Spring in the gorge | | 21·0 | 48·96 | 17·82 |
| 53 | Mema's Spring | | 20·6 | 9·005 | 3·278 |
| 54 | Klokoti | Carboniferous | 17·8 | 10·26 | 3·74 |
| 55 | Busovača | Oligocene | 12·8 | 0·6702 | 0·2497 |
| 56 | Vruća voda near Bugojno | Carboniferous | 25·1 | 5·813 | 2·116 |
| 57 | Ilidža near Hrušćica | Carboniferous | 19·5 | 2·181 | 0·794 |
| 58 | Ilidža near Tomina | Carboniferous | 29·9 | 11·28 | 4·107 |
| | Smrdelac near Jelovac | Cretaceous | | | |
| 59 | Upper Spring | | 12·6 | 3·605 | 1·312 |
| 60 | Lower Spring | | 13·1 | 5·812 | 2·067 |
| 61 | Gata Toplica | Triassic | 36·5 | 4·271 | 1·555 |
| 62 | Gornji Šeher | Cretaceous | 34·7 | 10·02 | 3·646 |
| 63 | Laktaši | Triassic | 30·4 | 0·4774 | 0·1738 |
| 64 | Slatina Ilidža | Cretaceous | 40·9 | 9·519 | 3·465 |
| 65 | Kulaši | Serpentine | 30·3 | 0·8273 | 0·3012 |
| | Vrućica near Teslić | Serpentine | | | |
| 66 | Thermal Spring | | 29·4 | 0·7609 | 0·2770 |
| 67 | Acidulated Spring | | 15·9 | 0·6430 | 0·2341 |
| 68 | Spring at Grabovica | | 14·5 | 0·6275 | 0·2284 |
| 69 | Dabravina | Triassic | 17·1 | 0·4050 | 0·1474 |
| 70 | Papratnica | Triassic | 12·8 | 1·455 | 0·5297 |
| 71 | Orahovica | Serpentine | 17·3 | 0·1940 | 0·0723 |

Table 1 (*continued*)

| Sample no. | Location | Stratigraphic age of source rock | Temperature (°C) | Radioactivity (Mache units) | Radioactivity (n c/l.) |
|---|---|---|---|---|---|
| | *Bosnia:* (*contd.*) | | | | |
| 72 | Acidulated Spring in Mala Rječica | Serpentine | 15·1 | 0·3720 | 0·1354 |
| 73 | Olovo | Triassic | 33·9 | 0·5961 | 0·2170 |
| 74 | Acidulated Spring in Prača | Carboniferous | 14·5 | 3·929 | 1·430 |
| 75 | Acidulated Spring near Derventa | Oligocene | 14·0 | 1·174 | 0·4273 |
| 76 | Sočkovac | Serpentine | 16·1 | 0·3503 | 0·1274 |
| 77 | Bokarić | Serpentine | 13·8 | 0·6412 | 0·2334 |
| 78 | Ilidža in Gradačac | Oligocene | 27·5 | 1·089 | 0·397 |
| 79 | Acidulated Spring in Jasenica | Eocene | 18·0 | 1·358 | 0·4943 |
| | Srebrenica | Carboniferous | | | |
| 80 | "Eye Water" | | 11·4 | 5·782 | 2·104 |
| 81 | Veliki Guber | | 12·4 | 17·19 | 7·02 |
| 82 | Mali Guber | | 13·7 | 9·829 | 3·578 |
| 83 | Velika Kiselica | | 12·4 | 9·505 | 3·460 |
| 84 | Mala Kiselica | | 14·1 | 7·997 | 2·911 |
| | Višegrad | Cretaceous | | | |
| 85 | Sokolović' Bath | | 34·2 | 6·951 | 2·530 |
| 86 | Caid's Bath | | 33·7 | 50·50 | 18·38 |
| 87 | Acidulated Spring in Jabuka | Carboniferous | 9·9 | 3·473 | 1·264 |
| 88 | Acidulated Spring in Bogušići | Carboniferous | 15·2 | 13·52 | 4·920 |
| | *Macedonia:* | | | | |
| | Banjsko | Pre-Cambrian | | | |
| 89 | Main Spring | | 71·8 | 4·846 | 1·764 |
| 90 | Spring of the Old Bath | | 56·7 | 4·460 | 1·623 |
| | Štip | Carboniferous | | | |
| 91 | Laundry Spring | | 66·8 | 42·42 | 15·59 |
| 92 | Bath Spring | | 50·3 | 11·57 | 4·213 |
| 93 | Well No. 6 | | 48·7 | 38·84 | 14·14 |
| 94 | Well No. 4 | | 64·2 | 45·56 | 16·58 |
| 95 | Well No. 3 | | 54·0 | 8·254 | 3·005 |
| 96 | Bogoslovac | Carboniferous | 9·4 | 9·194 | 3·346 |
| 97 | Katlanovo | Oligocene | 39·0 | 0·1903 | 0·0693 |
| 98 | Kočane | Pre-Cambrian | 56·5 | 8·02 | 2·92 |
| 99 | Projevo | Oligocene | 24·7 | 0·0586 | 0·0213 |
| | Konjsko | Pre-Cambrian | | | |
| 100 | Main Spring | | 11·2 | 0·5973 | 0·2174 |
| 101 | Spring No. 2 | | 14·4 | 1·188 | 0·432 |
| 102 | Gorničeto | Eocene | 25·5 | 0·4506 | 0·1238 |
| 103 | Negoračka Banja | Jurassic | 41·6 | 1·788 | 0·651 |
| | *Montenegro:* | | | | |
| 104 | Kalače near Rožaj | Permo-Carboniferous | 14·6 | 0·3168 | 0·1180 |
| 105 | Kralje near Andrijevica | Permo-Carboniferous | 10·2 | 0·7502 | 0·2731 |
| 106 | Igalo | Cretaceous | 14·8 | 3·71 | 1·35 |
| 107 | Ulcinj | Eocene | 14·1 | 1·90 | 0·693 |

In secondary enrichments of uranium low-rank coals are more effective in extracting uranium than any other material. Experiments by Moore (1954) showed that 98·0–99·9 per cent of the uranium is removed irreversibly from solution by such coals, probably as a metallo-organic compound, while clay, shale, and limestone keep only 16–28 per cent of the uranium contained in solution.

In the formation of the uranium deposits in the sedimentary rocks of the Colorado plateau the controlling factor is, according to Rosenzweig, Gruner and Gardiner (1954) the existence of a strongly reducing environment.

The thermal springs of Daruvar (Table 1, nos. 27–33) are typical vadose springs. Rains falling on the western slopes of Mt. Crni Vrh which culminates in the Dujanova kosa (830 m) and Ravna gora (856 m) pass through sediments belonging to the Upper Triassic of which the lower part (Karnian) consists of schists and is impervious to water, while the upper part (Norian limestones and dolomites) is permeable and serves as an aquifer. In Miocene the country was folded and the western part subsided along a N–S fault. The water is now carried in the aquifer to considerable depths and rises again along the fault to the surface. The bottom of the valley where the thermal springs are situated is covered with Pleistocene gravel in which the thermal water gets the character of ground water with the water table reaching 1–2 m below the surface.

The area of the thermal springs which is oriented SSW–NNE is elliptically shaped with the big axis of about 280 m and the small axis of about 60 m. On the SSW corner are the hottest springs (Anthony's Spring 45·9°C, Spring of the Central Bath 43·2°C, John's Spring 44·7°C) showing a low radioactivity (0·2369–0·3297 n c/l.). To the NNE where there are deposits of a black mud rich in $FeS_2$ (1·5–2 per cent) and colloidal particles on which the radioactive substances got adsorbed, the temperatures are lower: Spring of the General Mud Bath (37·0°C), Cold Spring (35·5°C), and the radioactivity rises sharply (1·750–1·850 n c/l.).

Although morphologically quite different, the conditions are geochemically similar in Istarske Toplice (Table 1, nos. 38–40). The country is built up by Upper Cretaceous limestone which is covered by Middle Eocene flysch (Salopek, 1954 and 1956). Part of the Upper Cretaceous (Turon) consists of dark bituminous limestone and contains 10–15 p.p.m. of uranium. The values were obtained by a calibrated Geiger counter and the counts obtained expressed as uranium equivalent (eU).

Farther south in the coal-mine of Raša some uranium from the limestone that has been carried away by circulating ground water was adsorbed in the beds of Eocene sub-bituminous coal, which in places yields up to 300 p.p.m. of uranium. A similar phenomenon has been described by Szalay (1954) for some sub-bituminous coals in Hungary, which in places contain up to 100 p.p.m. of uranium, by Breger and Schopf (1955) for the Upper Devonian Chattanooga shale in Tennessee and in the Cleveland member of the Ohio shale in Ohio, by Breger, Deul and Meyrowitz (1955) for the Eocene sub-bituminous uraniferous coal from the Red Desert, Sweetwater County, Wyoming and by Breger, Deul and Rubinstein (1955) for the Paleocene uraniferous lignite from the Mendenhall strip mine, Harding County, South Dakota. In all cases the uranium is associated with the organic components rather than with the minerals of the coal.

In Istarske Toplice the strata have been displaced by a NE–SW fault. The upthrown northern side forms now a fault scarp which is in places almost perpendicular. The displacement amounts to about 200 m. The fault was formed during the Eocene, as the flysch shows in places a phenomenon described by Beneo (1956) from the Appennines and called by him "*risedimentazione caotica*" (*argille scagliose*) as opposed to the normally stratified flysch. The phenomenon is due to a submarine slide which occurred during the faulting and thoroughly mixed the deposits. A similar phenomenon (*nappe de glissement*) has been reported from Morocco by Lévy (1952). The thermal sulphurous springs (21·4°C–31·6°C), which show a radioactivity of 43·30–50·05 n c/l. issue at the foot of the scarp. The bottom of the valley of the river Mirna is covered by some 10 m of alluvial deposits. To the west and south of the thermal springs there are extensive deposits of a black mud containing hydrogen sulphide and much colloidal matter. Here issues a cold spring (15·3°C) laid bare in 1955. It gives little water but shows a radioactivity of 218·5 n c/l., obviously due to secondary enrichment of radon in the radioactive black mud which contains 50–75 p.p.m. eU and through which the water seeps.

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# The absolute abundance of the nitrogen isotopes in the atmosphere and compressed gas from various sources*

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**Abstract**—The absolute abundance of the isotopes in atmospheric and commercial compressed $N_2$ from various sources has been determined. Nitrogen gas standards, prepared by mixing separated nitrogen isotopes in the form of $(NH_4)_2SO_4$ solutions, were employed to calibrate two 60° sector mass spectrometers. As a result, the absolute ratio of $N^{14}/N^{15}$ in atmospheric nitrogen was found to be 272·0 ± 0·3 Small variations from this value were found for commercial compressed gas.

The mass spectrometric procedure used in determining the $N_2^{29+}/N_2^{28+}$ ratio allowed for detection of differences to 1 part in 3500. However, the absolute accuracy of the abundance measurements was limited to 1 part in 1000 because of the semi-micro Kjedahl distillation employed to determine the amount of $(NH_4)_2SO_4$ present in the solutions of the separated isotopes.

In these measurements, instrumental background played a very significant role. A reliable method of correcting the observed $N_2^{29+}/N_2^{28+}$ ratio for the contribution of the background at these mass position was developed.

## Introduction

In 1950, Nier published a value of 0·366 % $N^{15}$ for the absolute abundance of the nitrogen isotopes of the atmosphere. His result was based upon calibration of two mass spectrometers with mixtures of separated $A^{36}$ and $A^{40}$. The basic assumption made was that instrumental discriminations for the nitrogen isotopes were proportional to those observed for the argon isotope mixtures. Two instruments were used by Nier, one employing a viscous leak and one a molecular leak. In the case of the former, the assumption was made that ratio measurements were distorted because of gas flow according to the square root of the masses being measured, and corrections for this were applied. In the latter instrument, no correction for gas-flow discrimination was applied, and the gas in the ion source was assumed to be representative of that in the inlet manifold.

The availability of highly enriched isotopes of nitrogen from ion exchange columns (Spedding *et al.*, 1955) at the Ames Laboratory of the Atomic Energy Commission presented the opportunity of using $N_2$ standards to re-examine the absolute abundance of the nitrogen isotopes in the atmosphere and in other sources. Use of nitrogen standards required only the reasonable assumption that any discrimination errors made in obtaining the $N_2^{29+}/N_2^{28+}$ ratio of the standards were of the same order of magnitude as those for the sample gas whose absolute $N_2^{29+}/N_2^{28+}$ ratio was to be determined. Thus the assumptions made are reduced to a minimum and the error which could result from a possible small difference in the ionization efficiencies of the molecular nitrogen isotope species was eliminated. Re-examination of the nitrogen isotope abundance problem seemed profitable in view of recent mass measurements (Ogata and Matsuda, 1953) of increased precision and the large range of values (265—274·5) which have been reported

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(Nier, 1950; Holt and Hughes, 1955; Schoenheimer and Rittenberg, 1939; Urey and Murphy, 1931; Wahl *et al.*,1935; Vaughan *et al.*, 1934; Soloway, 1951) for the $N^{14}/N^{15}$ ratio of atmospheric nitrogen.

## Experimental

### *Instruments*

Two mass spectrometers were used in these experiments. Both were equipped with dual ion current collectors and "viscous" leaks. One of the instruments, MS-1, was built here several years ago and, with only a few minor changes, was patterned after the design published by Nier (1947). Changes made were the elimination of plate $J_3$ in the ion source; mounting the ion source directly on the analyser instead of the tube flange; using Faraday cups instead of the flat plates for ion collectors and doubling the inverse feedback amplifier sensitivity by means of $8 \times 10^{10}$ Ω input resistors. The second instrument, MS-2, was a Consolidated–Nier, Model 21–201 (Consolidated Electrodynamics Corporation, Pasadena, California) which was unaltered from the specifications given in the manufacturer's handbook supplied with the instrument. Both instruments make use of the null method for comparing ion currents but have provisions for single ion current collection.

Any difficulties in making absolute abundance measurements which depend upon a precise knowledge of the linearity of the input resistors were eliminated by employing calibration standards whose ion-current ratios were very close to those of the samples being measured. The background in the two instruments in the mass positions 28, 29 and 30 were different. In MS-1, the background at 28 was 5 parts in 10,000 when a normal nitrogen pressure of 5·0 cm Hg was employed in the sample manifold, while that in MS-2 was 30 parts in 10000 under the same conditions. Backgrounds at the 29 and 30 positions in both instruments were 1–2 per cent of that in the 28 position. Because of the lower background, MS-1 was employed to assay the highly enriched $N^{14}$ and $N^{15}$ preparations. Only one collector was used in these analyses.

### *Preparation of the standards*

(1) *Assay of* $N^{14}$ *and* $N^{15}$ *solutions.* Gaseous nitrogen samples were prepared by the hypobromite oxidation of the $NH_4^+$ ions in the $N^{14}$ and $N^{15}$ solutions of ammonium sulphate obtained by neutralizing the eluant from the ion exchange columns. Isotope assays of $N_2$, prepared from these solutions, were made on MS-1 because the background at the 28, 29 and 30 mass positions was appreciably lower than it was in MS-2, thereby decreasing uncertainties due to background. Since peaks due to $N_2^{29+}$ and $N_2^{30+}$ were very small in the $N^{14}$ preparations, and peaks due to $N_2^{29+}$ and $N_2^{28+}$ very small in the $N^{15}$ preparations, corrections were made only for background and possible air contamination in the assay of these materials. Despite the fact that discrimination due to gas flow in the instruments probably existed in these cases, neglecting it introduced uncertainties in the results which had less effect on the mixed standards than did the Kjeldahl distillation used to determine the concentration of the $NH_4^+$ in the $N^{14}$ and $N^{15}$ solutions.

The constant for the expected distribution of the molecular species of nitrogen

based on a random combination of $N^{14}$ and $N^{15}$ should have a value of 4. This has been shown to be true at room temperature from quantum mechanical considerations (Urey and Greiff, 1935) for the equation $N^{28}{}_2 + N^{30}{}_2 = 2\ N^{29}{}_2$. It was experimentally demonstrated to be $3{\cdot}99 \pm 0{\cdot}01$ by work in these laboratories on mixtures containing 10–50% $N^{15}$ where the uncertainties due to background were negligible. As a check on the reliability of the isotope assay of both the $N^{14}$ and the $N^{15}$ preparations, a value for $K$ was computed from the observed 28, 29 and 30 ion peak heights. In both cases a value less than 4 was obtained, which indicated the possibility of small contaminations in the mass 28 and 30 positions. Because of the size of peaks at these positions in highly enriched $N^{14}$ and $N^{15}$ preparations, the value of $K$ is extremely sensitive to contaminants in the mass 30 and 28 positions, respectively.

In the $N^{15}$ preparations, small amounts of impurities in the mass 30 position had a negligible effect on the value of $K$. If contaminations at the 28 and 29 positions were assumed to be due to background and the presence of air, the 28 and 29 peaks could be corrected by observing the background after pumping out the sample gas and the $A^{40+}$ peak (Holt and Hughes, 1955) while the sample was in the instrument. Calculation of $K$ using the corrected values gave values very near to or slightly greater than 4·0. These small variations were attributed to random reading errors made while taking the data. Despite these precautions, the actual value of the per cent $N^{15}$ was changed less than 0·20 per cent in all assays made on the enriched $N^{15}$ preparations.

A small contamination in the mass 30 position had a similar effect on the value of $K$ computed from the observed peaks of the $N^{14}$ preparation. In assaying these materials, the height of the 30 peak was greater than would be expected from the measured 29 and 28 peaks. For this reason only the 28 and 29 peaks were used, along with an assumed value of 4 for $K$, to compute the isotopic constitution of the $N^{14}$ materials. No definite proof could be obtained that a contamination was not present at the 29 mass position. However, the consistent computed values of $K$ and the difficulty of postulating a plausible reaction to produce a species of mass 29 during either the hypobromite oxidation of the $NH_4{}^+$ ions or in the mass spectrometer while the sample gas was being assayed, seemed to indicate that the detectable $29^+$ mass current was produced solely by molecular nitrogen ions. A semi-micro Kjeldahl distillation was used to analyse these same $N^{14}$ and $N^{15}$ solutions for their total ammonium ion content. Numerous trial runs showed that the procedure gave consistent and accurate results to 1 part in 1000.

(2) *Mixing of the standards.* The carefully assayed $(NH_4)_2SO_4$ solutions were mixed by weight to prepare Standards no. 1 and no. 2, plus a series of solutions containing from 10 to 90% $N^{15}$. All of the information necessary to calculate the $N^{15}$ abundance in the two standards and other mixed solutions is tabulated in Tables 1 and 2. Deviations stated in these tables and all subsequent tables, except where noted, are average deviations. Standard deviations were calculated only when sufficient data warranted such calculations.

Portions of the no. 1 and no. 2 solutions were oxidized by the hypobromite reaction and the gases produced were used as standards to establish the absolute isotopic abundances of several sources of nitrogen. As subsequent tables show,

most of the measurements were made on MS-2, although, as mentioned earlier, the background at the 28 and 29 mass positions was much higher than on MS-1. This adverse effect of high background was partially compensated by the increased stability of MS-2 and the reliability of the background corrections, when these were necessary.

Table 1. Assay of solutions of $(NH_4)_2SO_4$ enriched in $N^{14}$ and $N^{15}$

| Runs | $(NH_4)_2SO_4$ enriched in $N^{15}$ | | $(NH_4)_2SO_4$ enriched in $N^{14}$ | |
|---|---|---|---|---|
| | Kjeldahl analysis mequiv/g solution $\times 10^4$ | At. % $N^{14} \times 10^3$ data from MS-1 | Kjeldahl analysis mequiv/g solution $\times 10^4$ | At. % $N^{15} \times 10^4$ data from MS-1 |
| 1 | 2398 | 198 | 2638 | 165 |
| 2 | 2393 | 207 | 2641 | 163 |
| 3 | 2393 | 212 | — | 165 |
| 4 | — | 207 | — | 166 |
| 5 | — | 210 | — | 176 |
| 6 | — | — | — | 152 |
| Average | 2395 ± 2·3 | 207 ± 4* | 2640 ± 1·5 | 165 ± 4·5† |

* This corresponds to 99·793 atoms % $N^{15}$
† This corresponds to 99·9835 atoms % $N^{14}$

If the magnitude of the 28 and 29 ion currents which yield the 29/28 ion ratios of both the standard and the sample gas whose abundance is to be determined are of the same order, then corrections for the background contribution to the observed ratios need not be applied. This ideal situation was achieved in most of the measurements by preparing Standards no. 1 and no. 2 (see Table 2) so that their isotopic abundance was near that of air and by removing the oxygen from the air samples by means of a mixture of sodium dithionite and the sodium salt of $\beta$-

Table 2. Data used in mixing calibration standards and test solutions

| Solution no. | Grams $N^{14}$ Solution taken | Grams $N^{15}$ solution taken | Calc % $N^{15}$* |
|---|---|---|---|
| Standard No. 1 | 35·83 | 0·1387 | 0·3657 |
| Standard No. 2 | 43·01 | 0·1983 | 0·4321 |
| 10 | 3·828 | 0·3997 | 8·650 |
| 20 | 3·343 | 0·8913 | 19·45 |
| 30 | 2·358 | 1·1081 | 29·84 |
| 50 | 1·4436 | 1·4433 | 47·47 |
| 60 | 1·4346 | 2·3687 | 59·85 |
| 60 | 1·2729 | 2·0803 | 59·60 |
| 70 | 0·9918 | 2·5664 | 69·99 |
| 90 | 0·4235 | 4·2093 | 89·83 |

* Absolute to 1/1000

anthraquinone sulphonic acid known as Fieser's solution (1924). This procedure has been shown to be non-fractionating by Soloway (1951), whose observation was corroborated here. Removal of oxygen improves the mass spectrometer stability during the measurements and aids in attaining higher precision. It also removes the potential production of CO by reaction of carbon with $O_2$ in the ion source. The alkaline nature of Fieser's reagent removes $CO_2$ which might also introduce a small error in the $29^+/28^+$ ratio measurement of atmospheric nitrogen. Then the absolute $N_2^{29}/N_2^{28}$ ratio of air ($O_2$ removed) or pure tank nitrogen was determined by comparison to the standard according to the following procedure:

(1) The mass spectrometer was conditioned with pure tank $N_2$ at 5 cm pressure for at least 2 h. This was necessary to stabilize the background in the desired mass region.

(2) The sample gas to be measured was introduced into the inlet manifold at $5{\cdot}00 \pm 0{\cdot}02$ cm pressure and 5–8 min were allowed before making any measurements.

(3) Four individual ratios were taken and the average of these was used as the observed ratio.

Three to five minutes were allowed for pump-out between samples and steps 2 and 3 of the above procedure were repeated in detail with the standard gas. The absolute ratio of the sample gas, ($R_t$), was then calculated, using the equation:

$$R_t = \frac{R_{\text{std. calc.}}}{R_{\text{std. obs.}}} \times R_{\text{sample gas obs.}} \qquad (1)$$

A series of measurements of the $N_2^{29+}/N_2^{28+}$ ratio of a sample gas containing impurities (5 % $O_2$) were made to prove that accurate comparisons with a standard could be obtained if corrections were made for instrumental background. To make this correction it was necessary to measure the $29^+/28^+$ ratio and the $28^+$ ion current of both background and the sample. Measurement of the latter was made at the time the ratio measurement was made. The $29^+/28^+$ ratio of the sample gas, ($R_s$), corrected for background contribution is given by

$$R_s = \frac{R_o - R_B(x)}{(1 - x)} \qquad (2)$$

where $R_0$ = the observed $29^+/28^+$ ratio; $R_B$ = $29^+/28^+$ ratio of background; $x$ = fraction of total 28 ion current due to background at the 28 mass position; $(1 - x)$ = fraction of total 28 ion current due to the sample gas. Table 3 shows the results of these measurements.

In this table, $R_1$ compares to $R_3$ within the limits of precision of the measurements. $R_2$ does not compare within these limits, due to the systematic error caused by failure to correct for the background contribution to the observed ratios. The observed $29^+/28^+$ ratio of 0·015 for the background in MS-2 contributed to the observed ratio of both the standard and the tank containing the $O_2$ impurity, but to a different degree, since the two gases were run at 5·0 cm total inlet manifold pressure. Thus the $R(t)$ as determined by equation (1) was high, due solely to the background.

If other contaminations are present in the sample, the error (caused by failure

to correct for the background when making comparisons to a pure standard at the same inlet manifold pressure) will depend upon (1) the per cent contamination, (2) the background ratio and (3) the magnitude of the $28^+$ ion current of the background with reference to the $28^+$ ion current due to sample gas.

It should be kept in mind when considering data presented in the next section of this paper that the Kjeldahl analysis limited the absolute accuracy of results to 1 part in 1000. Despite this fact, the method of comparing the $29^+/28^+$ ratio of two sample gases with a standard was capable of precision much better than 1 part in 1000 during any series of determinations. Consequently, the limits quoted in Tables 3, 4 and 5 are average deviations and are given as such in order to show the small variation in the $29^+/28^+$ ratio observed for nitrogen gas from various sources.

Table 3. $N_2^{29+}/N_2^{28+}$ measurements on commercial-tank $N_2$ containing 5% $O_2$*

| Run | $R_1 \times 10^6$ | $R_2 \times 10^6$ | $R_3 \times 10^6$ |
|---|---|---|---|
| 1 | 7358 | 7362 | 7355 |
| 2 | 7352 | 7353 | 7355 |
| 3 | 7355 | 7359 | 7351 |
| 4 | 7359 | 7363 | 7353 |
| 5 | 7355 | 7359 | — |
| 6 | 7356 | 7360 | — |
| 7 | 7357 | 7361 | — |
| 8 | 7363 | 7367 | — |
| 9 | 7361 | 7369 | — |
| Average | 7357 ± 2·6 | 7361 ± 3·1 | 7354 ± 1·5 |

* MS-2 was employed in these measurements and comparisons were made with Standard no. 1.
$R_1$—$O_2$ present, background correction applied to both standard and sample.
$R_2$—$O_2$ present, background correction not applied to either standard or sample.
$R_3$—$O_2$ removed by means of FIESER's solution; background correction not made.

Table 4. $N_2^{29+}/N_2^{28+}$ measurement on Matheson pre-purified $N_2$*

| Date | $R_t \times 10^6$ | Date | $R_t \times 10^6$ |
|---|---|---|---|
| 18 February 1957 | 7326 | 20 February 1957 | 7328 |
| 18 February 1957 | 7323 | 20 February 1957 | 7325 |
| 18 February 1957 | 7325 | 14 March 1957 | 7326 |
| | | Average | 7326 |
| | | Average deviation = 1·1 | |
| | | Standard deviation = 1·6 | |

* Measurements on MS-2; comparisons were made to Standard no. 1.

Table 4 gives six individual results of a series of determinations of the $29^+/28^+$ ratio for a tank of Matheson pre-purified nitrogen which was in our laboratory.

No corrections for background were necessary here, because comparison was made to Standard no. 1 and the gas was pure. This would also apply to the data in column four of Table 3. The standards applied to the data in Table 5 had 29/28 ratios which were very close to those of the pure nitrogen samples in question.

Table 5. $N^{29}{}_2{}^+/N^{28}{}_2{}^+$ measurements on $N_2$ from various sample gases*

| Nitrogen sample | Runs | MS used | Std. used | $R_t \times 10^6$ |
|---|---|---|---|---|
| Matheson† pre-purified tank | 6 | MS-2 | no. 1–6 runs | 7326 ± 1 |
| Matheson pre-purified tank | 5 | MS-1 | no. 1–3 runs<br>no. 2–2 runs | 7329 ± 6 |
| Linde purified tank | 3 | MS-2 | no. 4–2 runs<br>no. 3–1 runs | 7303 ± 4 |
| Linde purified tank | 4 | MS-1 | no. 3–4 runs | 7303 ± 5 |
| Puritan Sales‡ Commercial tank 5% $0_2$ | 4 | MS-2 | no. 1–4 runs | 7354 ± 2 |
| Oxidized $(NH_4)_2SO_4$ Baker and Adamson reag. grade | 4 | MS-2 | Matheson pre-purified tank | 7360 ± 1 |
| Air §, Ames, Iowa | 4 | MS-2 | Matheson pre-purified tank | 7352 ± 1 |
| Air §, Moosonee Bay, Ontario | 4 | MS-2 | Matheson pre-purified tank | 7351 ± 1 |
| Air §, 3000 ft above Kansas City, Missouri | 4 | MS-2 | Matheson pre-purified tank | 7351 ± 2 |
| Air §, 18,000 ft above Leavenworth, Kansas | 4 | MS-2 | Matheson pre-purified tank | 7350 ± 1 |
| Air §, 36,000 ft above Des Moines, Iowa | 4 | MS-2 | Matheson pre-purified tank | 7350 ± 2 |

* These analyses were made during the period starting 18 February 1957 and ending 30 May 1957.
† Summary of data presented in Table 4.
‡ $O_2$ removed by means of Fieser's solution; summary of data in Table 3, column 4.
§ $O_2$ removed by means of Fieser's solution.

Once again it was not necessary to apply background corrections to obtain these data. Table 5 shows the results for several commercial sources of nitrogen and air collected at various geographical sites and altitudes above these sites.

The no. 3 and no. 4 standards cited in Table 5 were prepared from solutions of ammonium sulphate less enriched in $N^{15}$ than those used to prepare the no. 1 and no. 2 standards. The results obtained with these standards showed that their calculated ratios were consistent with the no. 1 and no. 2 standards. Like the "Matheson tank", they are actually secondary standards and the agreement of the no. 3 and no. 4 with the no. 1 and no. 2 standards may have been fortuitous, since we had no absolute assurance that the mass spectrometric analysis of the $N_2$ gas prepared from the moderately enriched $(NH_4)_2SO_4$ solutions did not contain measurable discrimination errors.

From the abundance data for the nitrogen of the air given in Table 5, an absolute $N^{14}/N^{15}$ ratio of 272·0 ± 0·3 was computed. This compares favourably with Nier's value of 273 ± 1 for the same measurement. The present limits of

precision, however, produced a value for the physical atomic weight of nitrogen where the uncertainty in the calculated value was not due to uncertainties in the abundance data if the most recent mass measurements (OGATA and MATSUDA, 1953) for $N^{14}$ and $N^{15}$ were employed. The results of these calculations, in which NIER's value and the $N^{14}/N^{15}$ ratio of 272·0 ± 0·3 reported here were used, are given in Table 6.

Table 6. Physical atomic weight of nitrogen*

| $N^{14}/N^{15}$ ratio | Physical at. wt. |
|---|---|
| 273 ± 1 | 14·011190 ± 14 |
| 272·0 ± 0·3 | 14·011204 ± 4 |

* Masses of $N^{14}$ = 14·007551 ± 4 and $N^{15}$ = 15·004905 ± 6 of OGATA and MATSUDA (1953) were employed to calculate values given in this table.

The value of the chemical atomic weight is not affected by these results, due to the greater uncertainty of the conversion factor.

The results obtained on MS-1 and MS-2 for the various other mixtures of $N^{14}$ and $N^{15}$ solutions listed in Table 2 appear in Table 7. The amount of $N^{15}$ was calculated from the observed 28, 29 and 30 ion currents corrected for the background ion currents observed 3 min after pump-out of the sample gas. The amount of $N^{15}$ calculated after correcting the observed data for air contamination is also given as well as the results calculated when the observed data were corrected for gas flow discrimination using the assumption that the magnitudes of the observed ion

Table 7. Atoms per cent $N^{15}$ in mixtures made with separated isotopes.

| Calc. $\%N^{15}$* | *A* | | *B* | | *C* | |
|---|---|---|---|---|---|---|
| | MS-1 | MS-2 | MS-1 | MS-2 | MS-1 | MS-2 |
| 8·65 | 8·68 | 8·77 | 8·68 | 8·80 | 8·55 | 8·67 |
| 19·45 | 19·42 | 19·65 | 19·42 | 19·75 | 19·16 | 19·48 |
| 29·84 | 29·90 | 30·09 | 29·90 | 30·16 | 29·55 | 29·80 |
| 47·47 | 47·58 | 47·70 | 47·58 | 47·86 | 47·15 | 47·43 |
| 59·85 | 60·02 | 59·95 | 60·02 | 60·33 | 59·61 | 59·91 |
| 59·60 | 59·66 | — | 59·87 | — | 59·46 | — |
| 69·99 | 69·91 | 69·92 | 69·91 | 70·12 | 69·54 | 69·75 |
| 89·83 | 89·74 | 89·45 | 90·00 | 89·76 | 89·58 | 89·83 |

* Data from Table 2.
*A*—Corrections made for background at 28, 29 and 30 mass positions.
*B*—Correction made for background and air contamination based on measurement of $A^{40+}$ peak.
*C*—Correction made for background, air contamination and the assumption that the observed peak heights were distorted according to the square root of masses involved due to gas flow in the instrument.

currents are distorted according to the square roots of the masses under consideration.

In making the assays of the sample gases listed in Table 7, sufficient time for the background to stabilize was allowed after the sample was admitted and before data were taken. In a tight vacuum system, under conditions where no reactions take place in the instrument, the instability is due primarily to adsorbed gases. During this time, exchange takes place between the incoming molecules and those adsorbed in the various components of the instrument. An apparent elution of adsorbed gases takes place. This was indicated by the results of an experiment where purified argon (Gibbs *et al.*, 1956) was introduced into the mass spectrometer at 5 cm manifold pressure and the $28^+$ peak monitored. Immediately after introducing the argon, the height of the $28^+$ peak rose sharply, approximately doubling in size. Only after 10–15 min did the peak height fall to a size near its original value when it remained constant, even after pump-out.

The peak heights observed during any gas assay include ions originating from both sample and adsorbed gases. When assaying gases of varying composition in the instruments at this laboratory, 10–15 min were usually required before the spectrum stabilized. At this time the distribution of molecules representing the adsorbed gases approaches those of the sample. For this reason, any background corrections should be based upon peak heights measured after the sample has been pumped from the instrument. Consistent results are obtained in this manner and the background correction is reliable.

The data in Table 7 indicate that it may not be strictly valid to assume that gas flow in viscous leaks is the same for all leaks. Rather, gas flow may vary according to the exact conditions existing in particular instruments. The basic difference between MS-1 and MS-2 was that the amplifiers in the former were twice as sensitive as those in the latter. Since the mode of operation involved observing $28^+$ peaks of similar size on both instruments, the constriction at the end of the capillary comprising the "viscous leak" of MS-1 was smaller than that in MS-2. Sample pressure in the manifold was the same for both instruments, as were the lengths and diameters of the capillaries. The difference in constriction size was apparently great enough to alter sufficiently the flow characteristics in the capillaries, so that the simple assumption, that correction for molecular pump-out from the ion source can be made by using the square roots of the masses involved is not completely valid. Thus, flow through the leak in MS-1 was not purely viscous, while that through the leak of MS-2 probably was viscous. In the absence of calibrating media as presented here, corrections based on simple assumptions regarding the nature of gas flow in various mass spectrometer inlet systems may lead to greater uncertainties than those which might arise if no corrections were applied.

The close agreement between Nier's results for the normal isotopic abundance of the nitrogen isotopes and those reported here indicate that uncertainties in his basic assumptions were not great. However, deviations in other values for the isotopic abundances of nitrogen which have appeared in the literature are probably due to variations in gas-flow conditions existing in the various mass spectrometers on which those measurements were made, in addition to other discriminating factors which may result from source geometry.

## Summary

The abundance of the nitrogen isotopes in several sources of nitrogen has been determined. In atmospheric nitrogen the absolute ratio of $N^{14}/N^{15}$ is 272·0 ± 0·3. Small variations were observed in various sources of compressed gas. The abundance of the $N_2$ isotopes in air, which is constant to 1 part in 7000 in samples collected from various sites and altitudes, supports the findings of Dole *et al.* (1954).

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# The solusphere—its inferences and study*

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**Abstract**—Water is a fundamental geologic agent active in rock decomposition, erosion, and synthesis. Solutes in water are of particular interest to geochemists as sources of raw material for synthesis or as products of decomposition. When geochemical studies move from the laboratory into natural environment many variables relating to solute hydrology must be considered.

As a focal point there has been designed a graphical representation of solute hydrology, the solusphere, which embodies the concepts of land-water occurrence and movement on which are superimposed geologic, biologic, physical, chemical, and cultural processes affecting solutes. The solusphere is demonstrated by passing an imaginary plane through the centre of the earth. This plane intercepts concentric zones designated as rock flowage, saturation, aeration, surface activity, and atmosphere. Transport processes carry solutes within and between zones without alteration or conversion. However, whether stationary or in motion, the water's solute character is constantly subject to (1) alteration processes that change concentration by addition or subtraction of solutes or solvent without loss of solute identities, and (2) conversion processes that change the chemical state and form of solutes.

The geochemist is concerned with specific conversion processes, but he also must consider transport, alteration, and other conversion processes that are continually modifying the materials with which he is dealing in nature. The solusphere is an attempt to organize processes affecting the chemical quality of land waters into a unified field of science much like the field of marine chemistry.

In their studies of the rocks and minerals of the earth the geologist and the geochemist must always take into consideration the work of water. Success of deductions frequently is based upon correct interpretation of data on nature and amount of solutes in water. Yet not all water solutes are directly or solely related to the geology of the water environment.

Water is a fundamental commodity; it is the universal solvent, the most common medium in which changes in matter occur, the environment of most life processes, and a major transporter of material. Chemically pure water ($H_2O$) is rare, because in its predestined role on this planet water reacts with, takes up, holds, and discharges foreign material. Understanding of the occurrence of water solutes and use of observations are most difficult because of the variety, complexity and interrelations of the phenomena involved. Comprehensive organization is needed: (1) as a basis for correct interpretation of observed phenomena, (2) as a background in planning operational investigations, (3) for demonstration of the interrelationships of interests and multiple applications of knowledge available, (4) for recognition of deficiencies in knowledge of the total field and (5) as a guide to efficient means for conducting research. As one step in an attempt to fulfil this need there has been designed a graphical representation of the water environment and processes operating to affect water solutes. It has been named "solusphere" and is illustrated by Fig. 1. Not only is the solusphere an aid to conducting hydrologic investigations, but it also may help the geochemist give full consideration to the significance of water solutes as he conducts his studies.

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* Paper presented at second annual meeting of the Geochemical Society, Atlantic City, N.J., 6 November 1957.

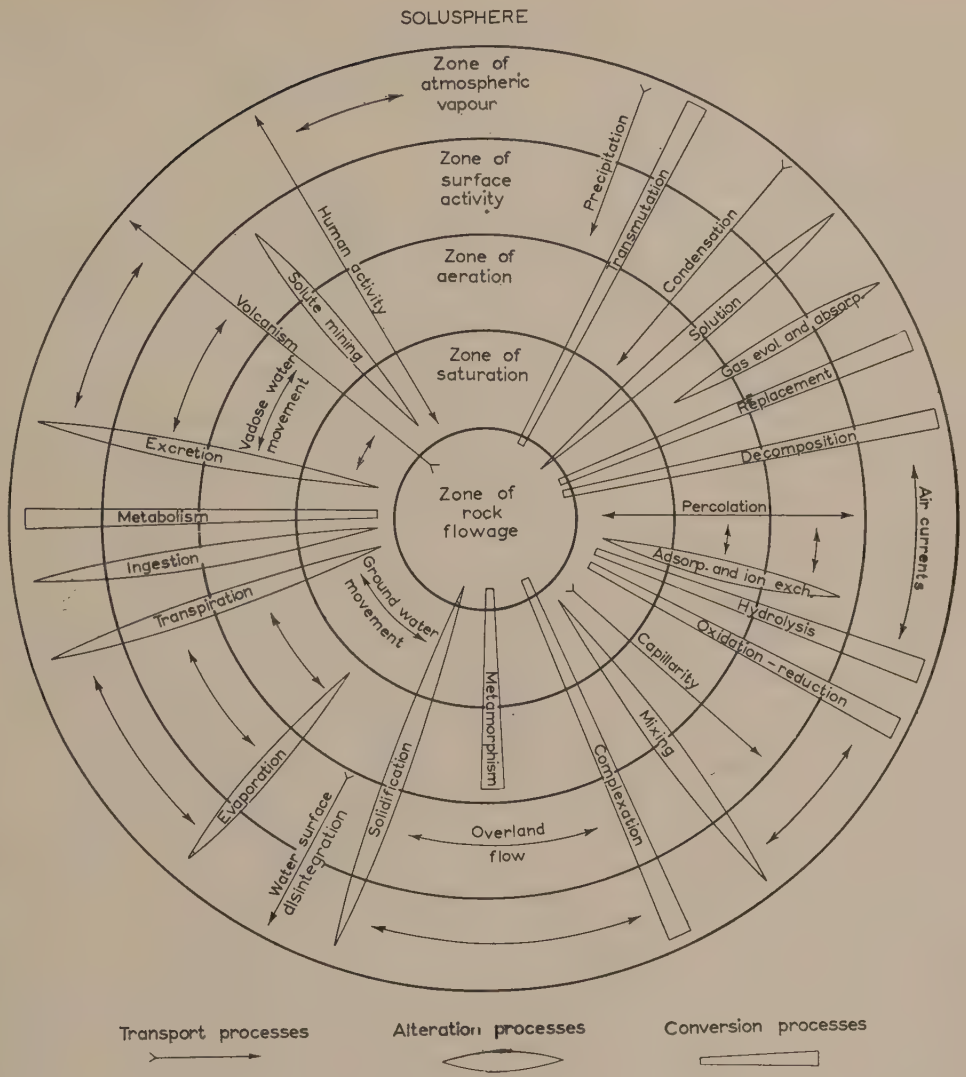


Fig. 1. The solusphere.

The solusphere is coincident with the occurrence and movement of water acting as a solvent. As a mental aid in visualizing the interrelation of processes affecting water solutes, imagine a plane passing through the centre of the earth and intercepting concentric zones of rock flowage, saturation, aeration, surface activity, and atmospheric vapour. Within and between the zones *transport processes* convey solutes from one place to another within the hydrologic cycle without alteration or conversion. However, the chemical characteristics of the water, whether it is stationary or in motion, are constantly subject to *alteration processes* that change concentration by addition or subtraction of solutes or solvent without loss of

solute identities, and also to *conversion processes* that change the chemical state or form of the solutes. The diagram shows the processes active in each zone. Solutes moving between zones are subject to processes intercepting the initial, intermediate, and terminal zones as shown on the diagram. Definitions of processes as used in the diagram are given in Table 1.

The hydrologic cycle (Meinzer, 1942) is useful in illustrating the occurrence and movement of water in nature, and the movement of earth material from one environment to another can be visualized in terms of the geochemical cycle (Hawkes, 1957). Similarly the solusphere is useful in illustrating the processes which may influence the solutes moving in these two cycles. However, the solusphere is not in any sense a cycle such as the hydrologic cycle or the nitrogen cycle. A cycle assumes change in position and/or state without net loss or gain of material. A "solute cycle" therefore would include most of the processes and states in which matter on earth is a part. In the solusphere only the occurrence of material in aqueous solution and the transport, alteration, and conversion processes affecting the solutes are considered.

Probably the most striking feature of the solusphere is the complex interrelationships it suggests. Although the existence of solutes is by definition coincident with the occurrence of water, the solute picture is complicated by factors not affecting quantity and movement of water as such. Neither measurement nor interpretation of chemical quality of water can be approached realistically without recognition of all the processes which might be significantly involved and the knowledge of their effects. Similarly geochemists and other investigators of conversion processes must be aware that transport and alteration processes are continually modifying the materials with which they are dealing in nature.

The point of view from which a process is observed may differ. In geochemical investigations, the weathering of biotite may be viewed as an origin of clay minerals, but the prime significance of the same reaction in water-quality investigations is as a mechanism for depletion of oxygen and addition of potassium, magnesium, iron, and silica to solution. Evaporation depression by surface films is receiving appreciable attention as a means of water (solvent) conservation, but it has a companion potential for minimizing concentration of solutes in lakes and reservoirs; in places of marginal quality, conservation of quality may approach or surpass conservation of quantity in importance. In well development the principal interest in iron precipitation may be its effect on aquifer permeability, but the solute character of the water also is altered by loss of iron from solution and the attendant increase in hydrogen-ion concentration. Only through recognition of the dual significance of many processes can hydrologic, geologic, and other investigations yield maximum benefit for the effort expended.

Another noteworthy feature of the diagram is the multi-zonal nature of many of the processes; the principal exceptions being the transport processes of air currents, overland flow, vadose-water movement, and ground-water movement. For example, the mechanics of adsorption and ion exchange are identical whether they are active in the saturation, aeration, or surface zones. This multi-zonal nature of processes emphasizes the potentiality of transposing available knowledge gained through study in one zone to problems in another zone. It also demonstrates

that pure research into basic processes inevitably will have widespread significance and application to investigations where water solutes may be involved.

In closely related fields the classification of some processes may be different from those given for the solusphere. For example, evaporation and transpiration are transport processes moving water but they are at the same time solute-alteration processes. In geochemistry, volcanism may be an alteration or conversion process that changes the distribution or composition of rock, but for the solusphere volcanism is a process by which matter is transported in aqueous solution. Adsorption and ion exchange alter the solute character of the water by adding and/or subtracting ions, but they are conversion processes from the standpoint of characteristics of the sediment particle.

The relative importance of a process to solvent vs. solute may differ widely. For example, animal life has little if any net significance in the hydrologic cycle, but the processes of ingestion, metabolism, and excretion as carried on in the world of bacteria and higher animals are very important in adding to, subtracting from, and changing the chemical state of solutes.

Few scientists can view the solusphere without being impressed by the voids and lack of balance in his knowledge of the total field. Yet many everyday problems require a comprehensive approach. Knowledge of the cause, nature, and effect of solutes in water has been built up piecemeal. Most studies have reflected the investigator's respective field of interest. The geochemist has been interested in solutes as they relate to changes in rock composition, the geomorphologist to modifications of landforms, the hydrologist to occurrence and circulation of water in the hydrologic cycle, the sanitarian to health, the industrialist to the economics and quality of his product, the plant physiologist to plant life, the soil scientist to soil texture and fertility, the ichthyologist to fish propagation, and the sociologist and economist to development of cultures and livelihood of population groups. A symposium on water solutes might bring forth a group of papers as varied as the proverbial blind men's descriptions of the elephant. Nevertheless, the solusphere is pertinent in its entirety to all studies that include solutes as one factor. Of course, the relative importances of the many processes differ from one situation to another, but one cannot assume magnitudes of significance without adequate evidence upon which to base his conclusion.

How can deficiencies, particularly in the poorly understood areas, be overcome most efficiently? The task probably is not as difficult as it first appears. If each process is considered individually, certain facts are evident. First, each process is part of some basic and rather well-developed science, such as chemistry, biology, meteorology, hydrology, or geology. Although studies in these sciences may not have been directed specifically toward water-solute problems, nor have been based on water-solute environment, the answers to many questions may be uncovered as by-products of investigations conducted for some other purpose. For example, studies of hydraulics of overland flow generally have not been concerned with material dissolved in water. Nevertheless, streamflow mechanics are a very important part of the investigation of water solutes. Likewise, oxidation-reduction has been studied extensively in inorganic and analytical chemistry, but the principles established have direct application to water solutes. Organization of

Table 1. Processes active in the solusphere

| Process | Type | Definition |
|---|---|---|
| Adsorption and ion exchange | Alteration | Reversible physical and chemical reactions between a gas, vapour, or solute and the surface of a solid. |
| Air currents | Transport | Motion of aeriform fluid. |
| Capillarity | Transport | The movement of a liquid in tubes or fibres brought about by attraction between the molecules both like and unlike. |
| Complexation | Conversion | The combination of substances that are themselves capable of independent existence. |
| Condensation | Transport | Transformation from vapour to liquid state. |
| Decomposition | Conversion | Process by which a substance undergoes disintegration. |
| Evaporation | Alteration | Vaporization that takes place at a temperature below the boiling point. |
| Excretion | Alteration | Act of discharging useless, superfluous, or harmful material from living plants and organisms. |
| Gas evolution and absorption | Alteration | Emission and taking up of a gas or vapour by by a liquid. |
| Ground-water movement | Transport | Motion of that part of the subsurface water which is in the zone of saturation. |
| Human activity | Transport | Man's modification of natural transport processes. |
| Hydrolysis | Conversion | A chemical reaction in which water acts upon another substance to form one or more entirely new substances. |
| Ingestion | Alteration | Used in the broad sense of taking in of nutrient and associated material by living plants and organsims. |
| Metamorphism | Conversion | The sum of thermodynamic processes of endogenetic origin which cause transformation of a rock into a well-characterized new type. |
| Metabolism | Conversion | The sum of processes concerned in the building up of protoplasm and its destruction incidental to life. |
| Mixing | Alteration | Processes by which two or more masses of water blend. |
| Overland flow | Transport | Drainage of water by flow over the earth surface. |
| Oxidation-reduction | Conversion | A chemical change in which the positive valence of an element is increased (oxidation) at the same time that the positive valence of another element, or of another portion of the same element, is decreased (reduction). |
| Percolation | Transport | Passage of a liquid under gravity or hydrostatic pressure through interstices. |
| Precipitation | Transport | Discharge of water in liquid or solid state out of the atmosphere. |

Table 1 (*continued*)

| Process | Type | Definition |
|---|---|---|
| Replacement | Conversion | Processes by which one chemical substance takes the place of some earlier different substances in an ion, molecule, or crystal lattice. |
| Solidification (chemical precipitation) | Alteration | Separation from solution as a solid. |
| Solute mining | Alteration | Extraction of solutes from water, particularly brines. |
| Solution | Alteration | The spontaneous formation of a homogeneous mixture of two or more substances subdivided down to molecular or smaller magnitudes. |
| Transmutation | Conversion | Reactions in which an atom is transformed into one or more of its isotopes or atoms of a different element. |
| Transpiration | Alteration | Process by which water escapes from the living plant into the atmosphere. |
| Vadose-water movement | Transport | Motion of that portion of the subsurface water which is in the zone of aeration. |
| Volcanism | Transport | Upward ejection of material as the result of thermal activity |
| Water-surface disintegration | Transport | Ejection into the air of water droplets by bursting bubbles and surface films. |

the solusphere by processes suggests that specialists in specific processes can contribute to the general knowledge of water solutes by research along lines of their academic or practical training. Second, the processes as related to water quality seldom include the entire basic science. For example, one does not have to be an expert in the entire field of physiology to be well versed on plant and animal life as it relates to solutes in water. Third, quantitative measurements in the field and laboratory are needed. It is not enough to know that certain complexation reactions occur or that precipitation transports solutes without learning also the magnitude of these processes as they operate in the solusphere. Again, techniques, or groups of them, may be found in other sciences that can be adapted with varying degrees of modification to quantitative measurements in the investigation of solutes in the hydrologic cycle. This has been done repeatedly in developing chemical techniques for water analysis.

Although there must be numerous approaches to surrounding and organizing the various factors in the total field, it is hoped that the diagrammatic presentation of the solusphere and the processes active therein will serve to clarify and stimulate thought and lead to wholesome development of a comprehensive and realistic approach in studies in which water solutes are a part. To the geochemist the solusphere may have specific value as a means of illustrating or suggesting factors that influence the interpretation of geochemical data.

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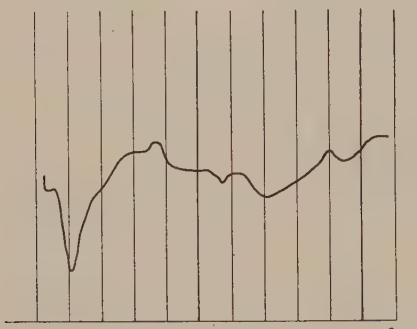
# Hydrogen (protium)-deuterium exchange in clays

J. Moum and I. Th. Rosenqvist

(*Received* 4 *February* 1958)

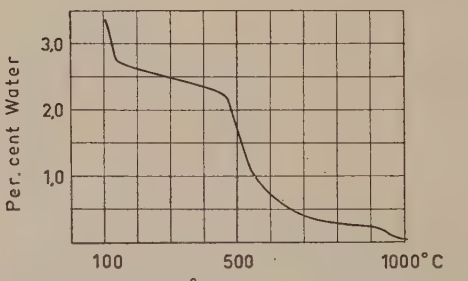
**Abstract**—The mobility of the hydrogen in clay minerals has been examined by exchange reactions with deuterium dioxide. It was found that the hydrogen of the clay minerals was present in three distinct states, each with its particular rate of exchange. The adsorbed water is exchanged in a matter of seconds or minutes; the $H_3O^+$ water in a matter of weeks, and the $OH^-$ water in a matter of years or even centuries.

Begemann and Libby (1957, p. 277) state from their analysis of tritium in rain water in the Mississippi valley, that on the average, about 8 m of ground water or equivalent including bound hydroxyl groups in clays are available for mixing with the rainfall. When Libby presented the result of these investigations at the




DTA of Åserum Clay

Fig. 1




Dehydratation of Åserum Clay dried at 110° C

Fig. 2

International Conference of the Radio Isotopes in Scientific Research, Paris, 9–20 September 1957, we gave a preliminary review of exchange reactions between D and H in clay minerals (Rosenqvist, 1957). The first series of these measurements are now finished and a full report can be given.

All the experiments were carried out with the blue postglacial inorganic clay from Åsrum, south-eastern Norway. This clay has an illite content of the order of 40 per cent, the rest being quartz, feldspar, etc. Base exchange capacity is 13·5 meg./100 g. The differential thermal curve is given in Fig. 1, and the dehydration curves in Fig. 2. The hydrousmicas have a formula of the type:

$$K_{2-y}(H_3O)_y\ Al_4(Si_6Al_2)\ O_{22}(OH)_4 nH_2O$$

In addition to the water of the mineral proper, some hygroscopic water is adsorbed. At room temperature and 96 per cent humidity, this corresponds to some 7 per cent of the dry weight. Even some of the water given off at temperatures above 110°C is considered to be hygroscopic. In addition to the adsorbed water, hydrogen is present as $H_3O^+$ and $OH^-$. This corresponds to the water given off at higher temperatures.

In order to examine the relative mobility of hydrogen in the different states, three series of measurements were performed. In the first series, a clay powder corresponding to the equilibrium state at room temperature and 96 per cent humidity (i.e. total water content 10 per cent) was used. About 7 per cent of the water is given off between room temperature and 110°C. This clay powder was mixed with a surplus of $D_2O$ containing water, and immediately afterwards the water was filtered off in a vacuum filter. The whole procedure could be carried out in 53 sec. Afterwards the specific gravity of the redistilled filtrate was determined by the falling drop method.

From the change in gravity, the exchange between water added and the mineral water could be determined. The result could, however, never be sufficiently accurate because of the large amount of mixing water necessary. The result was that 100 per cent $\pm$ 30 per cent exchange had taken place between the added water and the water adsorbed hygroscopically between room temperature (humidity 96 per cent) and 110°C (humidity 0·6 per cent).

In the next series of experiments, we started with a clay dried at 110°C. This clay had a total residual water content of 3·30 per cent. 25 g of this clay powder was mixed with 1 g of water containing $D_2O$ to a specific gravity 1·01107 (20°/40), and subsequently the mixture distilled at 110°C after various times and the first drops collected. The $D_2O$ content of the water distilled off was determined and recalculated as percentage of the value for total mixing between the added water and the total hydrogen in the minerals. The following values were found (Table 1).

Table 1. Room temperature 20°C

| Storage time (min) | Exchange (%) |
|---|---|
| 10 | 7·6 ± 3 |
| 120 | 14·4 ± 2 |

Table 2. Temperature 110°C

| Heating time | Exchange (%) |
|---|---|
| 0–1 hour | 13·3 ± 2 |
| 3 days | 13·3 ± 2 |
| 34 days | 24·7 ± 2 |
| 46 days | 30·4 ± 2 |
| 78 days | 30·4 ± 2 |
| 610 days | 36·0 ± 2 |

The exchange values are plotted in Fig. 3

In a third series, 10 g samples of clay dried at 110°C were mixed with 1 g of water containing $D_2O$ and melted off in reagent tubes. The tubes were placed in an oven at 110°C. After various periods of heating, the tubes were opened and the specific gravity of the water which could be distilled at a temperature of 110°C, was determined and recalculated as percentage of the asymptote value as mentioned above. The values obtained are shown in Table 2.

As seen from the exchange rates, the hydrogen of the clay may be divided into at least three different groups: (1) The hydrogen which undergoes very quick exchange reactions with the surrounding water. (Asymptote value 13 per cent of the water in the 110°C dried clay.) This amount of water corresponds to roughly

the amount of water given off between room temperature at 96 per cent humidity, and 160°C. (2) The hydrogen which undergoes a slow exchange reaction with the surrounding water phase (asymptote value 30 per cent of the water in the 110°C dried clay). (3) Hydrogen which undergoes a very slow exchange reaction even at

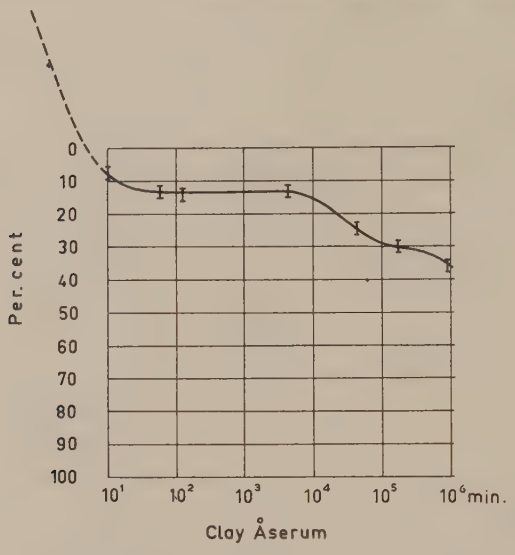



Fig. 3

Exchange of H/D in per.cent of H content at 110°C

temperatures of 110°C. (The asymptote value for this exchange is not reached in 610 days.)

According to this data, one may assume:

13% of the hydrogen content at 110°C is adsorbed
17% of the hydrogen content at 110°C is in $H_3O^+$ positions
70% of the hydrogen content at 119°C is in $OH^-$ positions

The formula of this mineral at 110°C would be:

$$K_{1\cdot67}(H_3O)_{0\cdot33}\ Al_4(Si_6Al_2)(OH)_4\ 0\cdot37(H_2O)$$

The exchange ratios indicate that it is the $H_3O^+$ water which is exchanged at a time of weeks, whereas the $OH^-$ water will need years or centuries even at elevated temperatures. There should, therefore, be no reason to believe that the tritium content of rain water will be influenced by the hydroxyl groups in the clay materials when the water passes through the ground as ground water. The only water available for such an exchange seems to be the free ground water and the adsorbed water. In the case of montmorillonites, the temperature at which the $OH^-$ water is expelled may be even higher than in the case of illites; this will probably involve an exchange as slow as found by us.

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# GEOCHEMICAL NOTE

## Information needed with analytical data*

(*Received* 8 *January* 1958)

THE ranks of the geochemists are widening, and geologists are being presented with invaluable data at an accelerating rate. As both the quality and the quantity of such data increase, we are correspondingly challenged to make proper use of them. Much of that use must depend upon the accompanying geologic information, but the needed information is too often lacking from papers by both geologists and geochemists. Illustration will be made by reference to chemical analyses and absolute-age determinations.

We are past the stages at which the utility of chemical analyses is limited to the shotgunning of points on simple variation diagrams or to the calculation of conventional norms or similar numbers, although such treatment is quite adequate for many studies. Interrelationships between chemistry, mineralogy, occurrence, and genesis of rocks must receive increasing scrutiny, but such scrutiny is not possible where adequate descriptions of the rocks are lacking. Similarly, comparisons with rocks of other areas must be made in terms of petrography and occurrence as well as bulk composition.

*A chemical analysis should be accompanied by a precise location, a brief statement of occurrence, and a petrographic description of the specimen.* A mode is of course desirable if the mineralogy and grain size permit counting. To give any less is to forfeit much of the potential of an expensive analysis. There may be little point in getting an analysis at all if it is to be discarded with only the common "an analysis of a typical specimen is presented in Table 3", the "typical" meaning perhaps only that the specimen was unweathered.

If more refined field studies, or studies over a large area, or absolute-age determinations require revision of rock-unit designations or of inferred geologic histories, it should be possible to use the previous analytical data in terms of the new information, and not to be forced to reject the data for the lack of description.

What *can* be done with chemical data? Far more uses will occur to future workers than to us, but even so the following are only a few problems now being studied which require knowledge of rock descriptions, locations, and field relationships. What variations and relationships are there within a suite of rocks, or between suites, defined either broadly or specifically on any combination of criteria of mineralogy, chemistry, occurrence, texture, location, age, etc.? Where, mineralogically, are the elements in a rock? Why do igneous rocks of nearly identical composition develop widely varied textures and mineralogy in different environments? What rocks previously assumed to belong to single groups are actually members of diverse suites? What changes accompany metamorphism? There are many more such problems.

When chemical data are used to supplement aerial studies, estimates as to the relative abundances of the rocks analysed are valuable. The frequency distributions of rock elements in various areas and provinces may tell much about the possible genesis of the rocks, but frequency studies cannot be made satisfactorily from specimen suites which emphasize the uncommon rocks unless rock proportions can be integrated.

A paper in which geologic considerations are secondary to the chemical but which has fine rock descriptions is that by SHAW (1956). Each of the new analyses of medium- and high-grade metapelitic rocks is accompanied by a counted mode, a location, and a description of which this is a sample (p. 923):

> L62 Staurolite schist
>
> A silvery crumpled schist. Porphyroblasts of staurolite, with quartz-graphite inclusions, and of occasional garnets, in a matrix of quartz, muscovite, and biotite, with crumpled schistosity planes. Staurolite crystals have been fragmented by shearing along micaceous folia. Principal opaque mineral is graphite, but iron oxides are also present. Minor feldspar and sphene. Grade: staurolite zone.

Given this information, no one wanting to use SHAW's analysis will be in doubt as to what was analysed.

The mechanical presentation of analytical data greatly affects the ease with which it can be understood, and the scheme of presentation should be logical in terms of the items tabulated. The system followed by BUDDINGTON (1939) for the presentation of analytical, calculated, and petrographic data is an excellent one. In continuous tables, BUDDINGTON presented chemical analyses, norms, and modes, and beneath these on the same sheet the description and location. Having all of these together much simplifies comparisons between them. BUDDINGTON used tipped-in folded sheets for the longer tables, but the same result could generally be achieved with single quarto pages or with facing octavo pages.

Few papers give the needed information as well as do the two just cited. It would be unfair to single out for critical citation a few papers from the majority in which description and location are inadequate. Most papers give only sketchy rock descriptions, or none at all but only rock names; in some papers, even the names are of questionable validity. Locations are usually given in only the most general terms. The analyses in such papers can be used for little more than characterizing gross chemical features of petrographic provinces.

The pedigree of an analysis should be indicated also. The analyst's name and brief address, and the year of analysis, should be specified, as "analysis by H. B. Wiik, Geological Survey of Finland, Helsinki, 1954". Giving the analyst's name permits judgement of the quality of an analysis and appraisal of the comparability of different analyses. Giving the place and date may give clues on procedures used and on the location of more detailed records.

Most of the radiocarbon absolute-age determinations now being published are accompanied by specific descriptions adequate to make them most useful to other workers, as in this sample from a long list (OSTLUND, 1957, p. 494):

> *Lund.* Relics of tree roots (*Alnus* or *Betula*), found at Måsvägen 18, in glacial sand covered by 1·3 m of Baltic moraine and underlain by northeastern moraine. The sample was taken 1·5 m below the surface. No traces of similar roots were seen in the covering Baltic moraine. In spite of this, the sample evidently represents postglacial tree roots. Submitted by H. Möller.

Such information is rarely given for absolute-age determinations of rocks, however, and without such information it may be impossible to interpret the determinations geologically.

*An age determination should be accompanied by a precise location, and by a brief petrographic description and a statement of relations to other rock units.* The description of the Swedish radiocarbon sample given above is a model of the sort of information needed, less the petrography. A locality designated only as a mine or a quarry will be insufficient for everyone but the few geologists intimately familiar with the area. Studies of suites of specimens from geologically well-known areas—for example, as done in the fine paper by

Evernden, Curtis and Lipson (1957) for the granitic rocks of the Yosemite region—are generally much more valuable than are determinations of near-random specimens.

Without description, it is often impossible to tell what rock is being dated, and whether the date gives the likely age of formation of that rock or instead a spurious age due to subsequent alteration of the rock. For an extreme example recently published, a date, however good, for an unnamed rock located only as from "Colorado" is not informative, as the Pre-Cambrian terrain of Colorado includes granitic and metamorphic rocks of complex histories and widely diverse ages. It is imperative that the material dated be specified adequately to prevent confusion. This is particularly obvious with the Precambrian terrains, in which polymetamorphism and repeated intrusions over long spans of time are common.

Giving geologic and petrographic information with analytical data will greatly increase the utility of that data for little added effort. A dividend may often accrue when the preparation of this information causes a re-evaluation of unstable assumptions about the genesis and field relationships of rocks.

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## Book review

Henri and Genevieve Termier: **L'Evolution de la Lithosphere. I: Petrogenese.** 653 pp., 40 figures, 54 plates. **II: Orogenese;** in two parts, 940 pp., 152 figures, 54 plates with 86 Maps representing an Atlas of Structural Geology. Masson & Co., Paris, 1956. Price, bound, each volume 9,800 fr.

The authors have undertaken a remarkable and most impressive task in writing a new, comprehensive treatise of geology. The intent and purpose are to explain genesis and evolution of the lithosphere by interpretative studies of geological phenomena. This original series of publications cannot fail to receive the most signal welcome by everybody interested in geology.

The first volume, *Petrogenesis*, has been reviewed by me;* it discusses the outstanding problems of petrogenesis and the evolution of rocks in connexion with the crust of the earth, and with the structure of matter in general.

The second volume, *Orogenesis* (in two fascicules), is concerned with the history and evolution of the singular orogenic zones in the crust of the earth that are, or will become, the prominent mountain chains of the world.

The volume on orogenesis, part I, starts with a discussion of the actual movements of the crust, earthquakes and the depths of the earth. Then follow an introduction to structural analysis, basement tectonics, thrusts, infrastructure tectonics with special emphasis on vertical and tangential movements.

* (1956) *Geochim. Acta* **10**, 244.

Part II deals with the ocean basins, rather briefly, and mainly restricted to descriptive facts.

Parts III and IV deal with the continents of Laurasia and of Gondwana.

Part V deals with the Tethysian orogeneses, i.e. the salient mountain chains of Europe, North Africa, Asia and Central America. These are areas which have been closely studied by a great number of geologists, and the reader will find compiled a lot of information that will be of great help for future studies.

Part VI is an essay on megatectonics (in the sense of BUCHER): the natural classification of orogens according to their mode of evolution and mutual connexions; new ideas are developed like relay movements between contiguous orogens, captures, and unison of action.

In my review of the first volume (*Petrogenesis*) I called it a work of inspiration. I will repeat this after having read the volumes on orogenesis. It is an enormous work of compilation and references and an outstanding contribution to geological sciences.

T. F. W. BARTH

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## Papers to appear in future issues

The next issue of this journal, Vol. 14 No. 4, will contain the papers contributed to a Symposium on Tektites, held in Washington in June 1957, under the auspices of the National Academy of Sciences and the National Research Council. The following papers will appear:

E. L. KRINOV: Some considerations of tektites.

VIRGIL E. BARNES: Properties of tektites pertinent to their origin.

ALVIN J. COHEN: The absorption spectra of tektites and other natural glasses.

JOHN H. RINEHART: Impact effects and tektites.

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